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Synthesis and Lithography of Colloidal Nanomaterials

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Los Alamos National Laboratory, Los Alamos, NM

Connecticut College, New London, CT
November 12th, 2014

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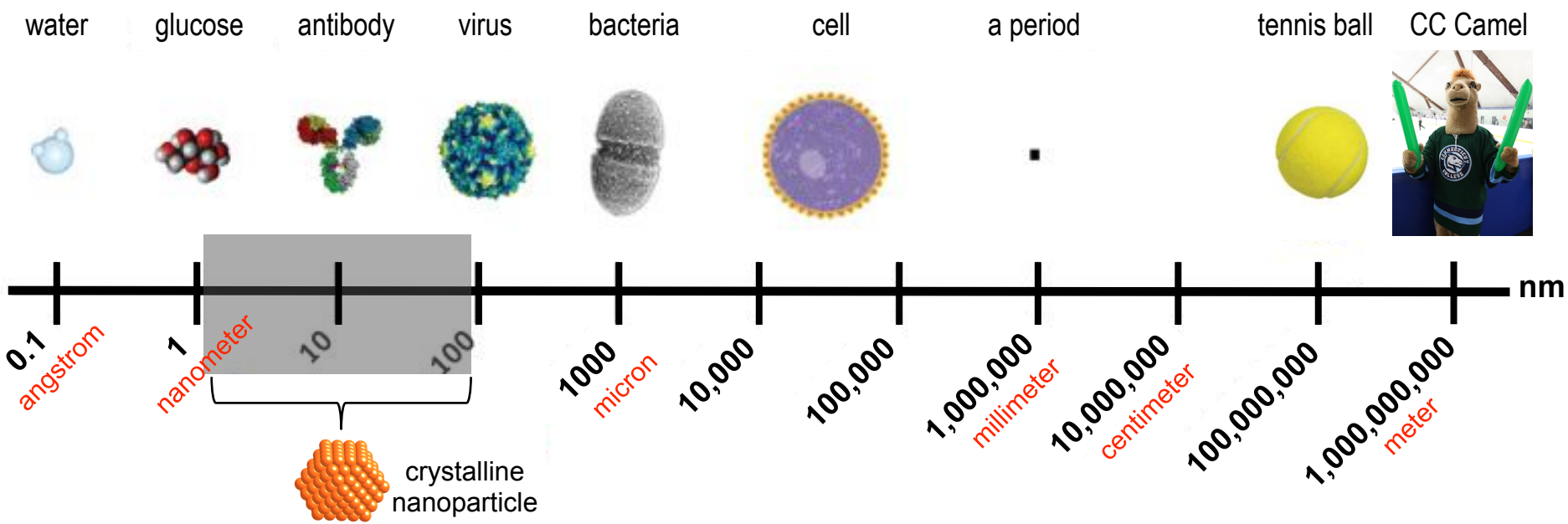
What are Nanomaterials?

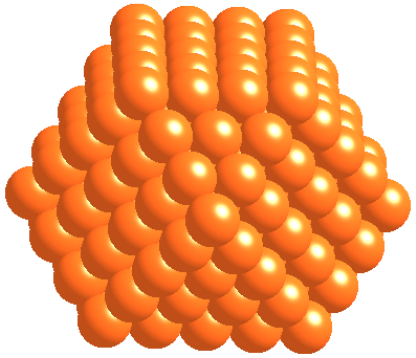


Materials that have dimensions in the 1-100 nanometer range

Inorganic Materials
"Bulk" Gold vs. "Nano" Gold

gold bar

>>> 6.022×10^{23} total atoms

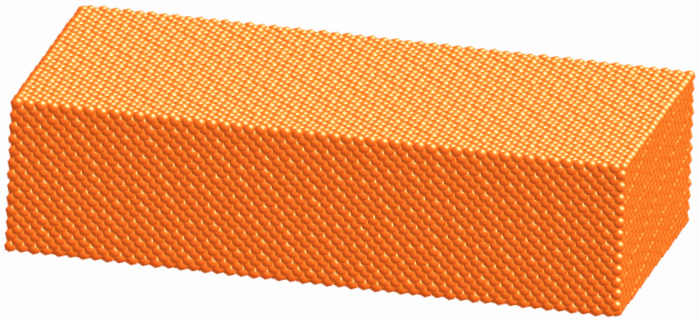


gold nanoparticle

100-1000 total atoms

http://www.usagold.com/gold/coins/bars.html

Differences between Bulk and Nano



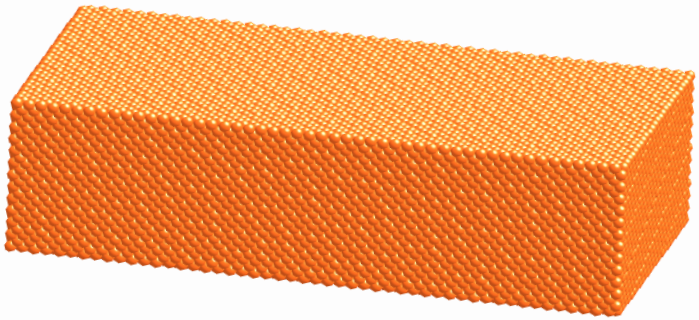
low surface to volume ratio

gold bar

http://www.usagold.com/gold/coins/bars.html

http://nanocomposix.com/collections/gold

Differences between Bulk and Nano



low surface to volume ratio

$$\frac{\text{\# of surface atoms}}{\text{\# of total atoms}}$$

gold bar

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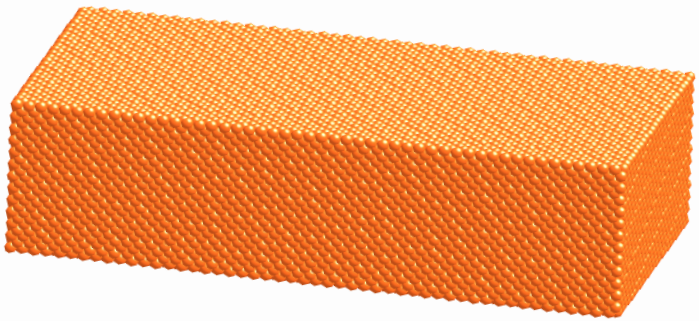
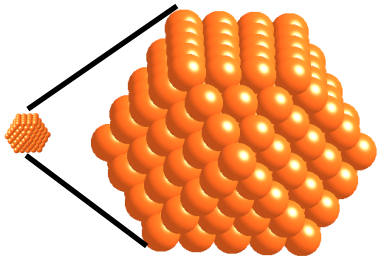


low surface to volume ratio



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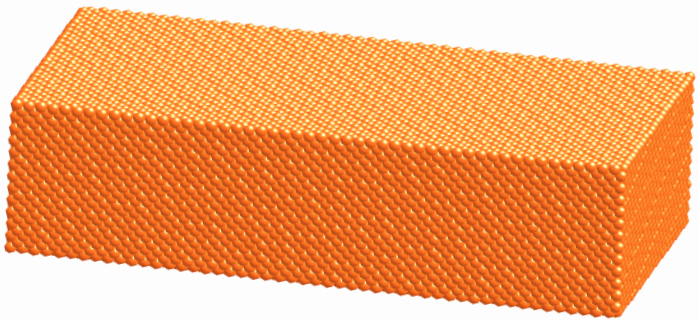
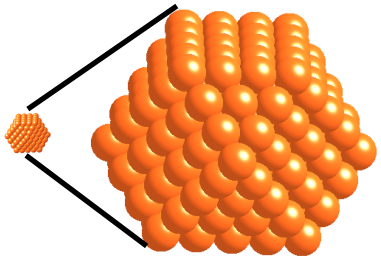


low surface to volume ratio

$$\frac{\text{\# of surface atoms}}{\text{\# of total atoms}}$$

<<<



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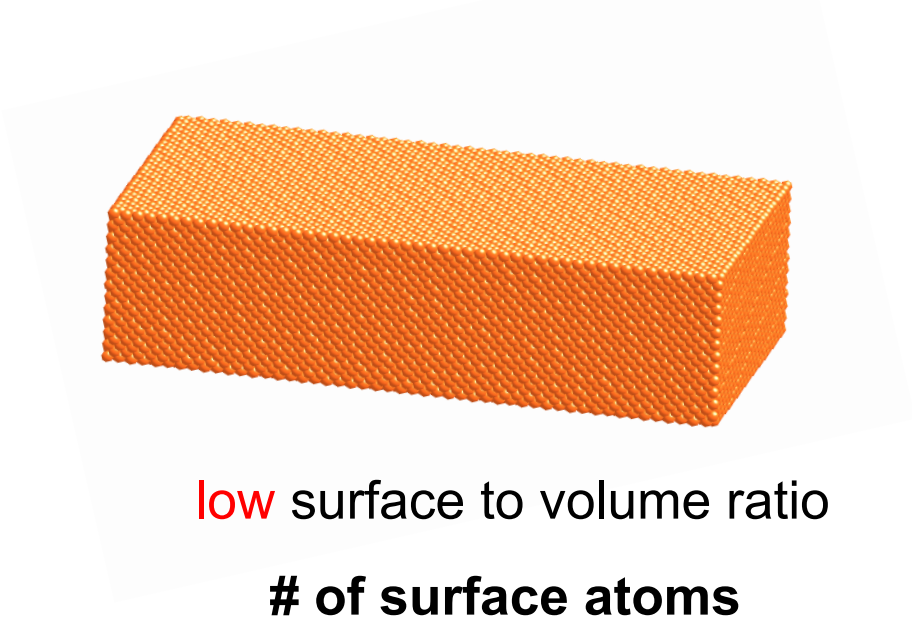

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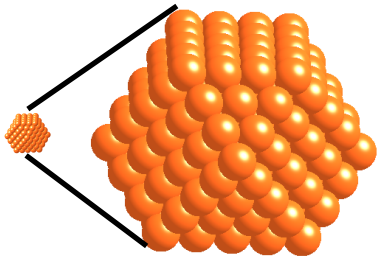

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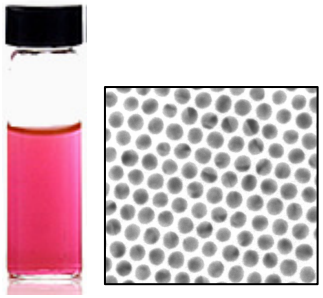

gold nanoparticles in solution

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http://www.usagold.com/gold/coins/bars.html

http://nanocomposix.com/collections/gold

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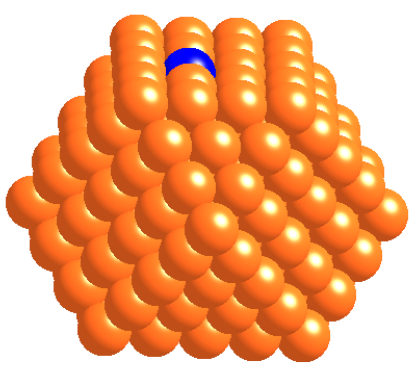
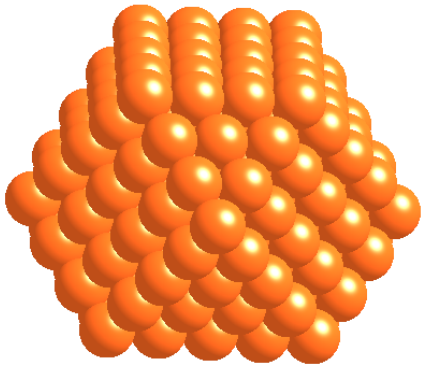
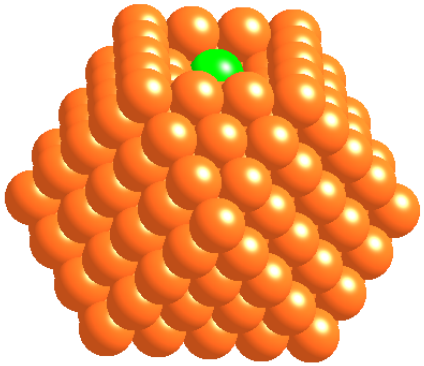
The Significance of Surface Atoms

surface atom





interior atom



- not fully coordinated
- higher energy
- higher degrees of freedom
- give rise to surface-related properties

- fully coordinated
- lower energy
- do not contribute toward surface-related properties

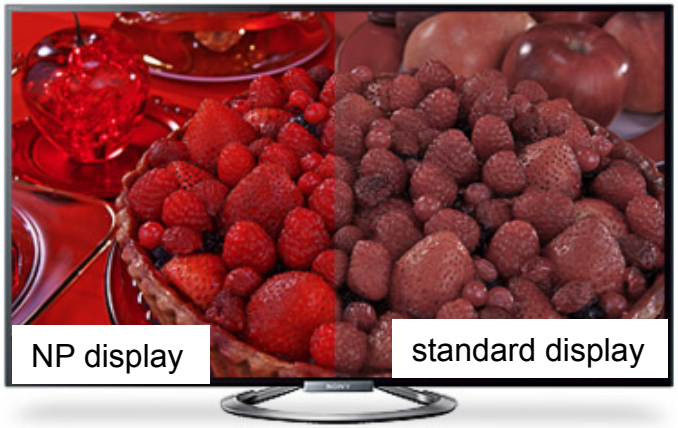
Size-dependent Properties of Gold Nanoparticles

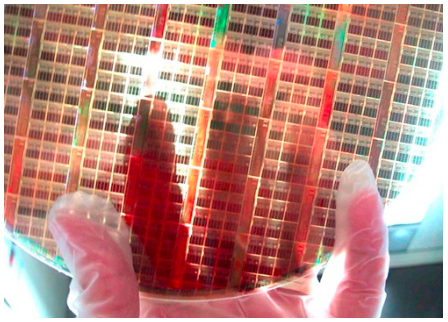
relative surface area decreases

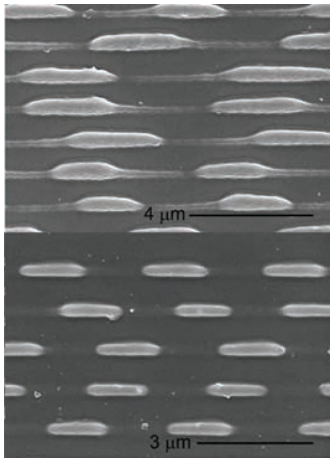
The **# of surface atoms** on a nanoparticle affects the color of the gold solutions due to ***surface plasmon resonance***

Applications of Nanomaterials

semiconductor nanoparticles for displays



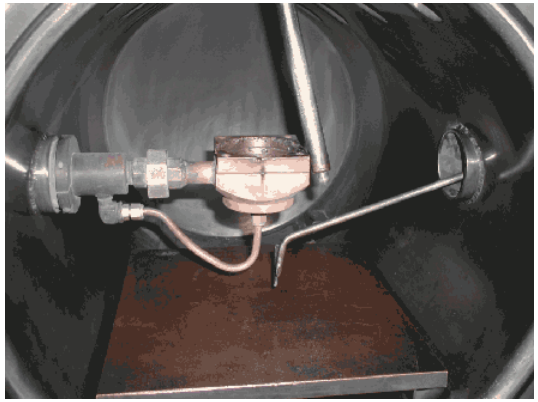


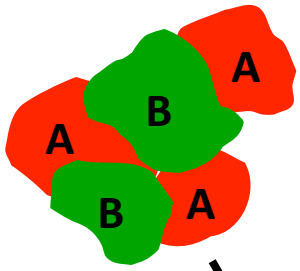


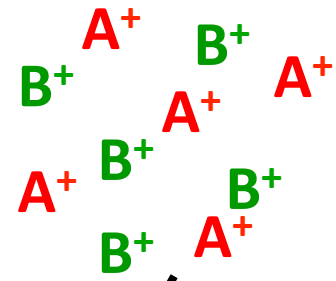
lithography for smart electronics

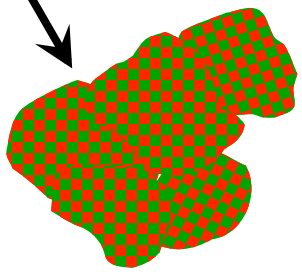
http://www.nanotech-now.com/news.cgi?story_id=29788
http://www.sony.co.in/TVP-LCD-TV/range/TRILUMINOS-Series/562831
http://www.qset.us/solar-energy/photovoltaic-power-plant/
http://www2.chem.umd.edu/groups/fourkas/publications.html
http://optics.org/news/1/2/12/IBM3Dsmall

Synthesis of Nanoparticles

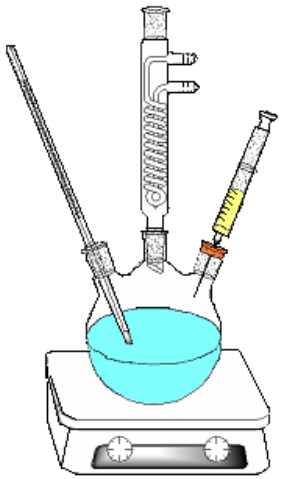








AB nanoparticle



"Top-Down" approach

High temperatures

fractioning of larger particles

<u>Solid-solid diffusion is the rate limiting step</u>

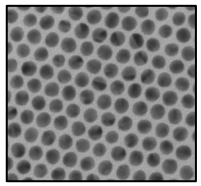
Alternative "Bottom Up" approaches <u>eliminate solid-solid diffusion as rate-limiting step</u>

Low temperatures and solution methods result in milder conditions "colloidal"

Liquid-Phase "Colloidal" Synthesis of Nanoparticles

$$\text{Precursor}_{(solv)} \underset{\pm e^-}{\overset{\Delta}{\rightleftharpoons}} \text{Monomer}_{(solv)} \rightleftharpoons \text{Nanocrystal}_{(s)}$$

nucleation



soluble metal salts, metal complexes, other reagents

Transient species; complexed atoms or ions, molecular fragments, clusters

Klimov, V. *Semiconductor and Metal Nanocrystals: Synthesis and Electronic and Optical properties.* Marchel Dekker New York **2004.**

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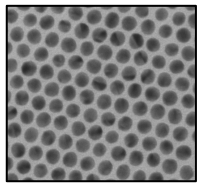

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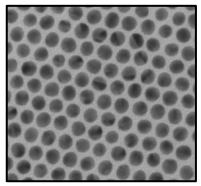

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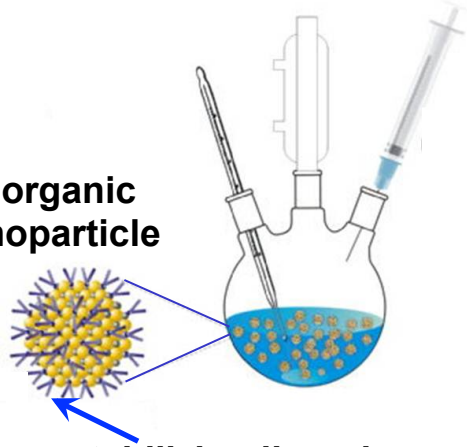


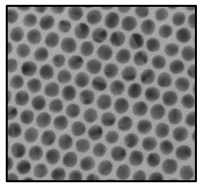
Inter-molecular forces between surface stabilizing ligands and solvent allow nanoparticles to remain suspended

- **truncate and mediate nanoparticle growth**
- **impart solubility and processability**

Liquid-Phase "Colloidal" Synthesis of Nanoparticles

Precursor $_{(solv)}$ $\xrightleftharpoons[\pm e^-]{\Delta}$ **Monomer** $_{(solv)}$ $\rightleftharpoons$ **Nanocrystal** $_{(s)}$

nucleation



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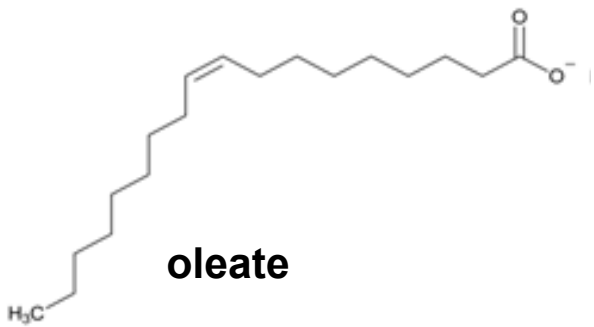

oleate

Inter-molecular forces between surface stabilizing ligands and solvent allow nanoparticles to remain suspended

surface-stabilizing ligands passivate surface atoms of nanoparticles

- **truncate and mediate nanoparticle growth**
- **impart solubility and processability**

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Klimov, V. *Semiconductor and Metal Nanocrystals: Synthesis and Electronic and Optical properties.* Marchel Dekker New York **2004.**

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Liquid-Phase "Colloidal" Synthesis of Nanoparticles

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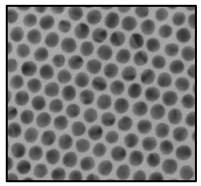

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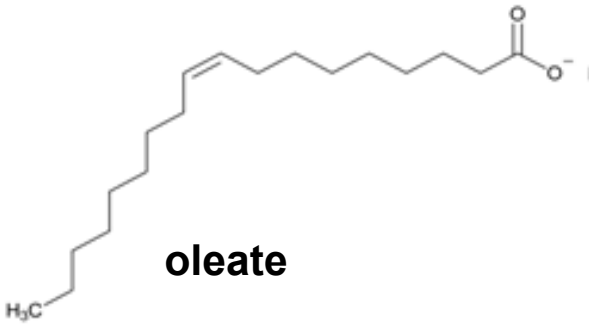

oleate

Inter-molecular forces between surface stabilizing ligands and solvent allow nanoparticles to remain suspended

- **truncate and mediate nanoparticle growth**
- **impart solubility and processability**

- **not materials general**
- **ideal for transition metals, metal oxides**
- ***multi-element nanoparticles are difficult to synthesize***

surface-stabilizing ligands passivate surface atoms of nanoparticles

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Klimov, V. Semiconductor and Metal Nanocrystals: Synthesis and Electronic and Optical properties. Marchel Dekker New York **2004.**

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Need Alternative Strategy to Synthesize Nanoparticles

Nanoparticle "Conversion Chemistry" Methods

Outline

Part I: Template-directed Colloidal Synthesis of Metastable Inorganic Nanoparticles

- Mechanism of Colloidal Synthesis
- Accessing Metastable Phases

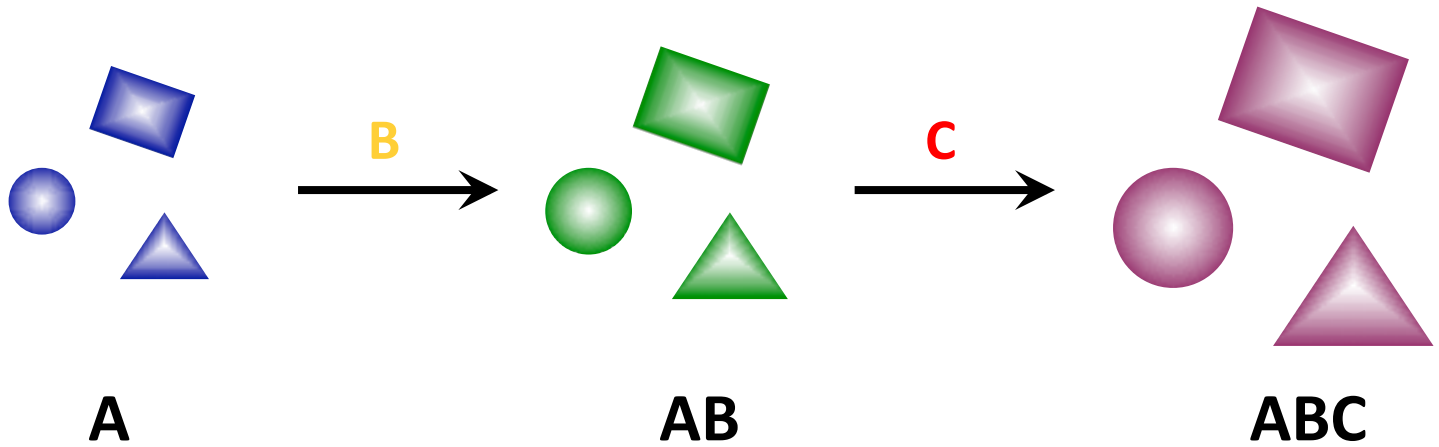
Part II: Dip-Pen Nanolithography of Colloidal Nanoparticles on Sub-micron Surfaces

- Semiconductor Nanoparticles
- Dip-pen Nanolithography

Nanoparticle "Conversion Chemistry" Methods

Templating

"when one material behaves as a model or pattern to help generate a consistent product"



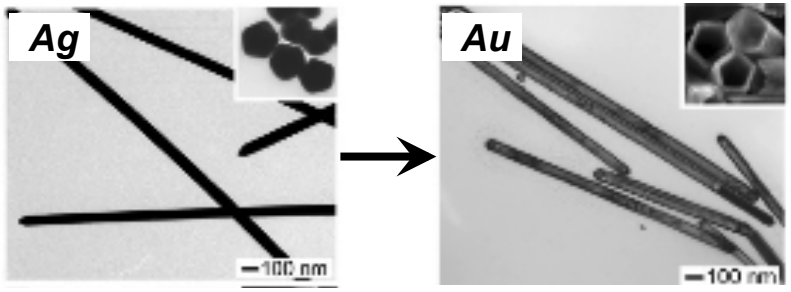
"easy-to-synthesize" nanoparticles are used as reactive templates to synthesize complex, multi-element nanoparticles

Previous Work on Template-Based Conversion

Templating

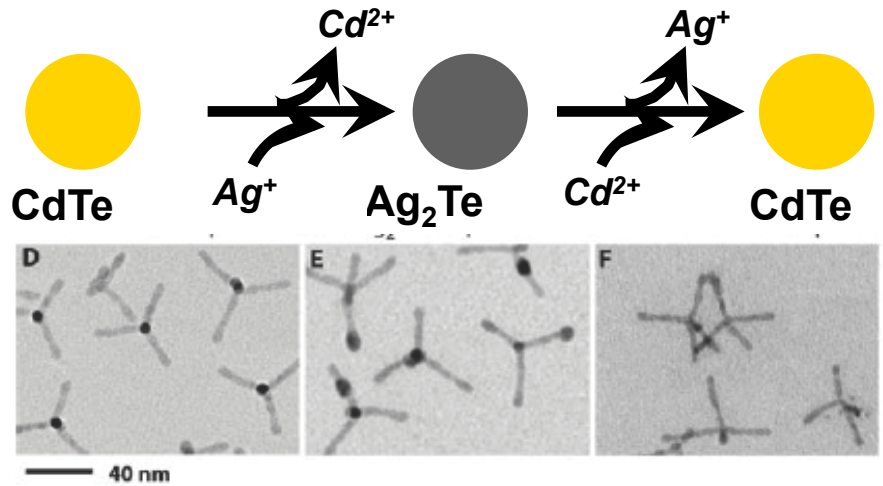
"when one material behaves as a model or pattern to help generate a consistent product"

$$3Ag_{(aq)} + AuCl_4^-{}_{(aq)} \rightarrow Au_{(s)} + 3Ag^+{}_{(aq)} + 4Cl^-{}_{(aq)}$$



Galvanic Displacement

Cation Exchange

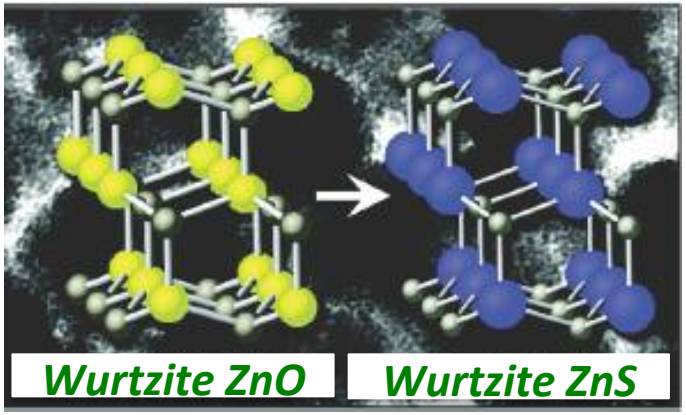


Robinson, R.; Sadtler, B.; Demchenko, D. O.; Erdonmez, C. K.; Wang, L.; Alivisatos, A. P. *Science* **2007**, *317*, 355-358.
Sun, Y.; Xia, Y. *J. Am. Chem. Soc.* **2004**, *126*, 3892-3901.

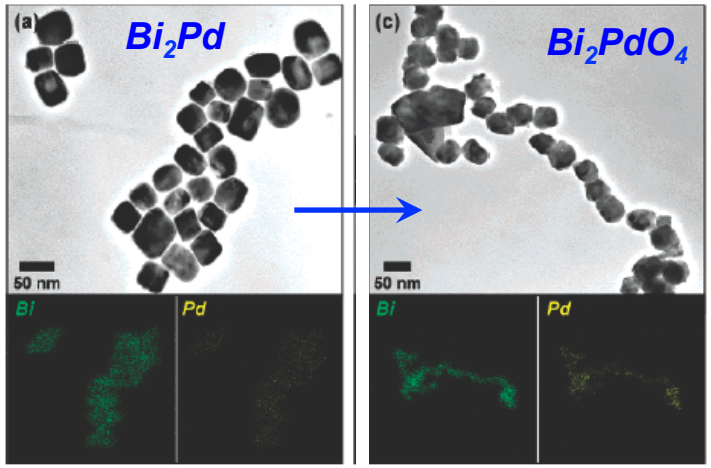
Reactive Templating Methods

pre-formed nanocrystals are converted/incorporated into final product

1. Crystal Structure



2. Chemical Composition



Access new/metastable materials

Allows for predictability of final product

Pre-determined characteristics of final product

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Dawood, F; Leonard, B. M.; Schaak, R. E. *Chem. Mater.* **2007**, *19*, 4545-4550.
Dawood, F.; Schaak, R. E. *J. Am. Chem. Soc.* **2009**, *131*, 424-425.

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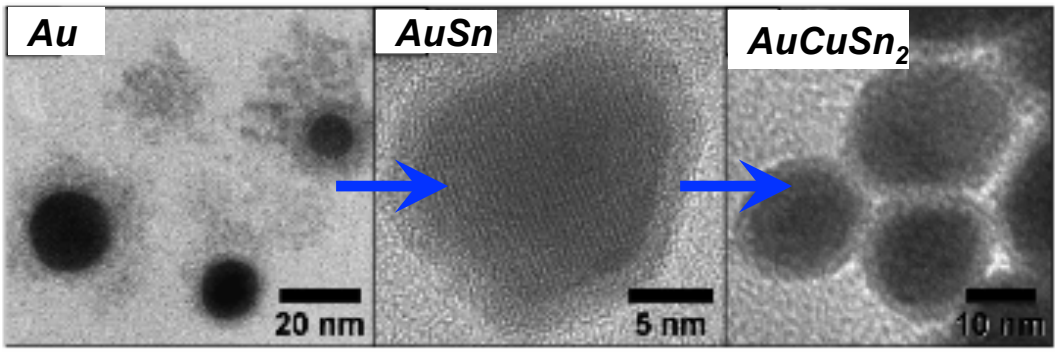
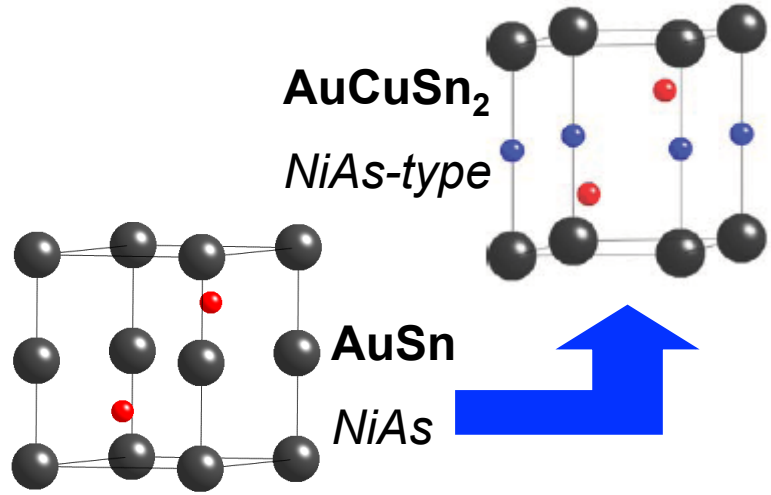
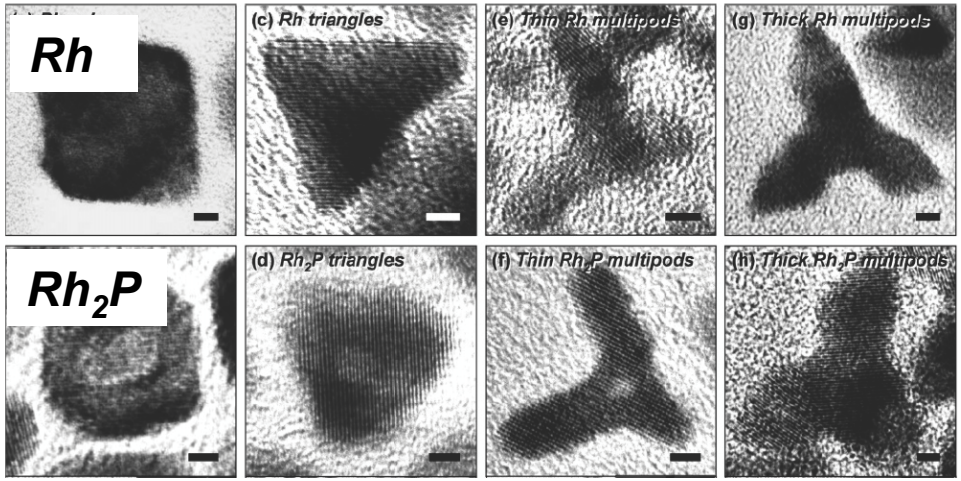
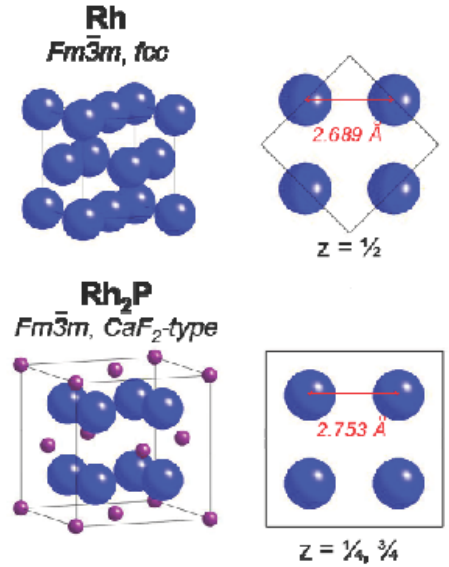
1. Crystal Structural Templating



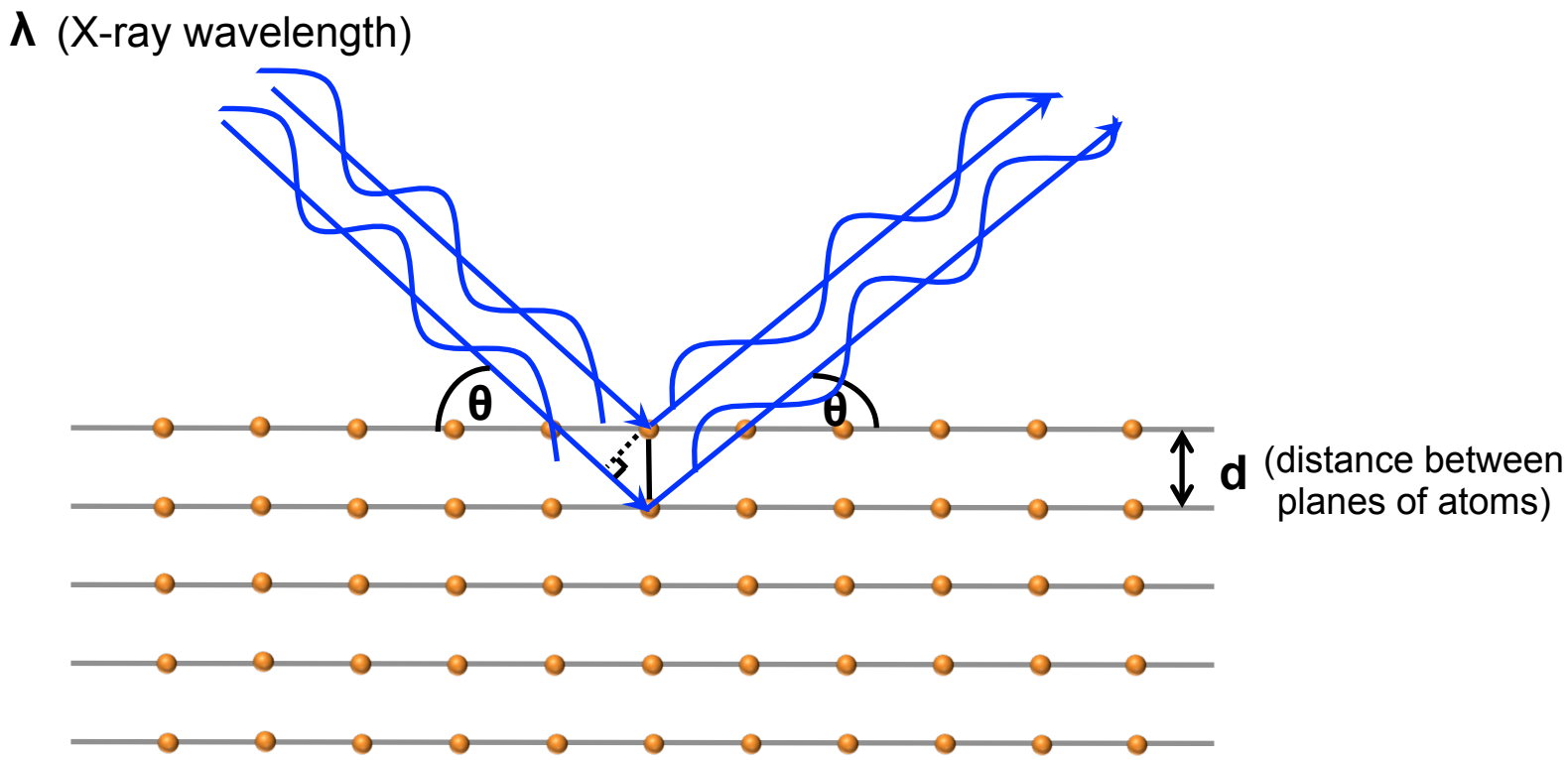






Leonard, B. M.; Schaak, R. E. *J. Am. Chem. Soc.* **2006,** *128*, 11475-11482.
Henkes. A. E.; Schaak, R. E. *Inorg. Chem.* **2008,** *47*, 671-677.

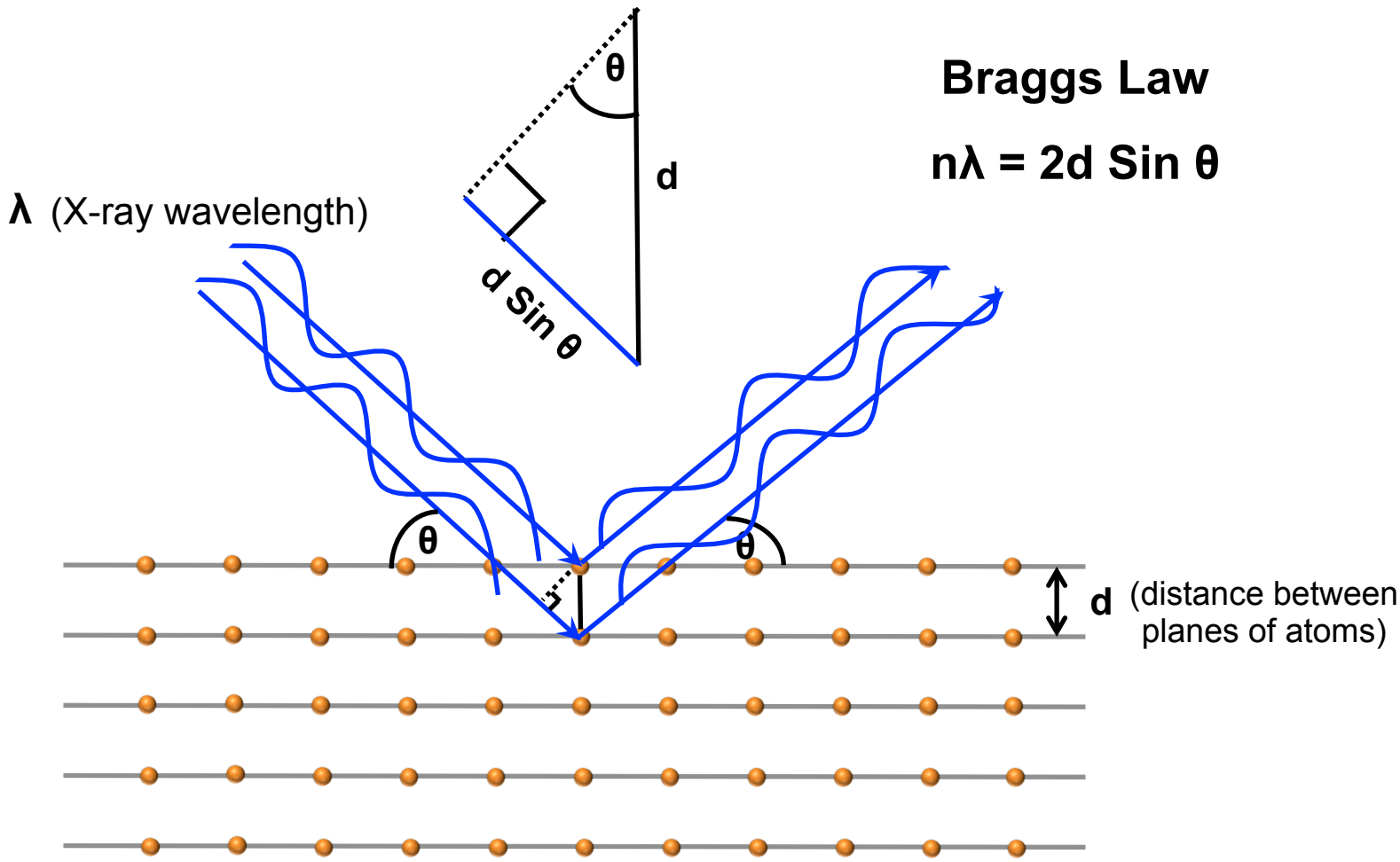
Powder X-ray Diffraction



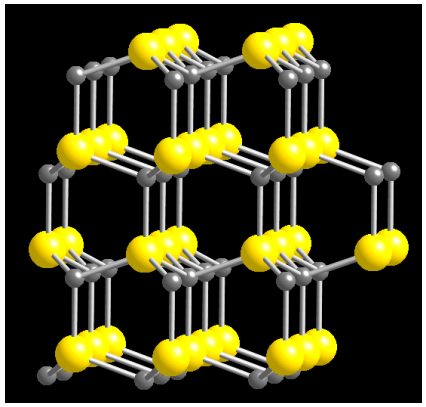
Powder X-Ray Diffraction

Braggs Law

$n\lambda = 2d \sin\theta$

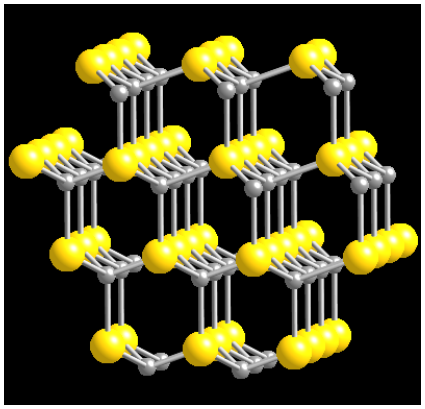


Exploring ZnS



Wurtzite (WZ) hcp

wider band gap
thermally stable above 1000 °C



Zincblende (ZB) ccp

forms more easily
more stable at RT (~10.25 kJ mol^{-1})

- WZ and ZB have very similar crystal structures
- Both have similar powder X-ray diffraction patterns
- Wide bandgap semiconductors
- Reaction pathway for formation of WZ nanocrystals not fully understood

Qadri, S. B.; Skelton, E. F.; Dinsmore, A. D.; Hu, J. Z.; Kim, W. J.; Nelson, C.; Ratna, B. R. *J. Appl. Phys.* **2001**, *89*, 115–119.
Wang, Z.; Daemen, L. L.; Zhao, Y.; Zha, C. S.; Downs, R. T.; Wang, X.; Wang, Z. L.; Hemley, R. J. *Nat. Mater.* **2005**, *4*, 922–927.

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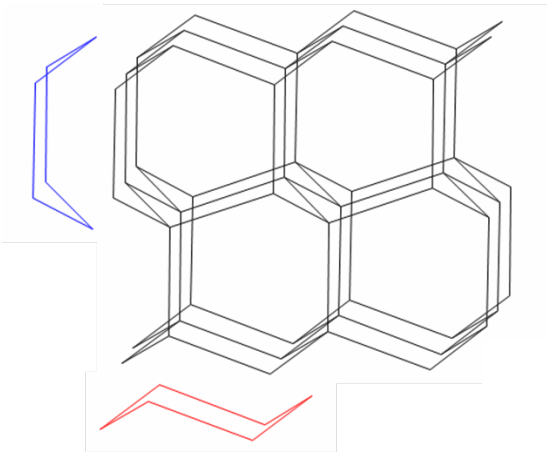
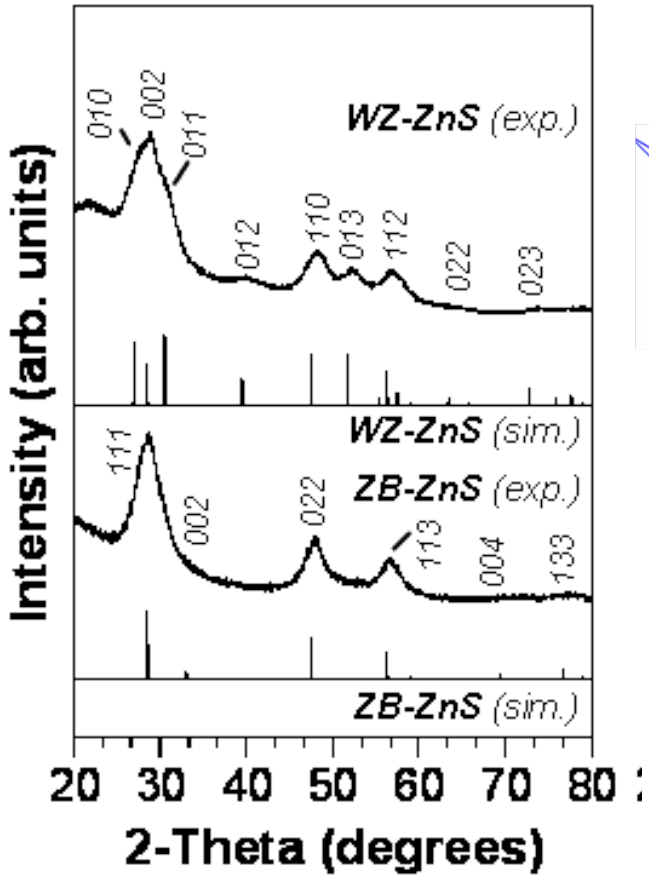
Comparison of Wurtzite and Zincblende of ZnS

Wurtzite (WZ)

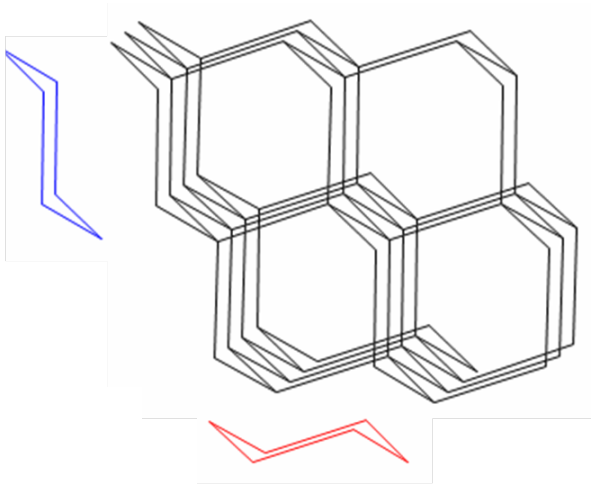


ABABAB

3.80 eV



Zinc Blende (ZB)



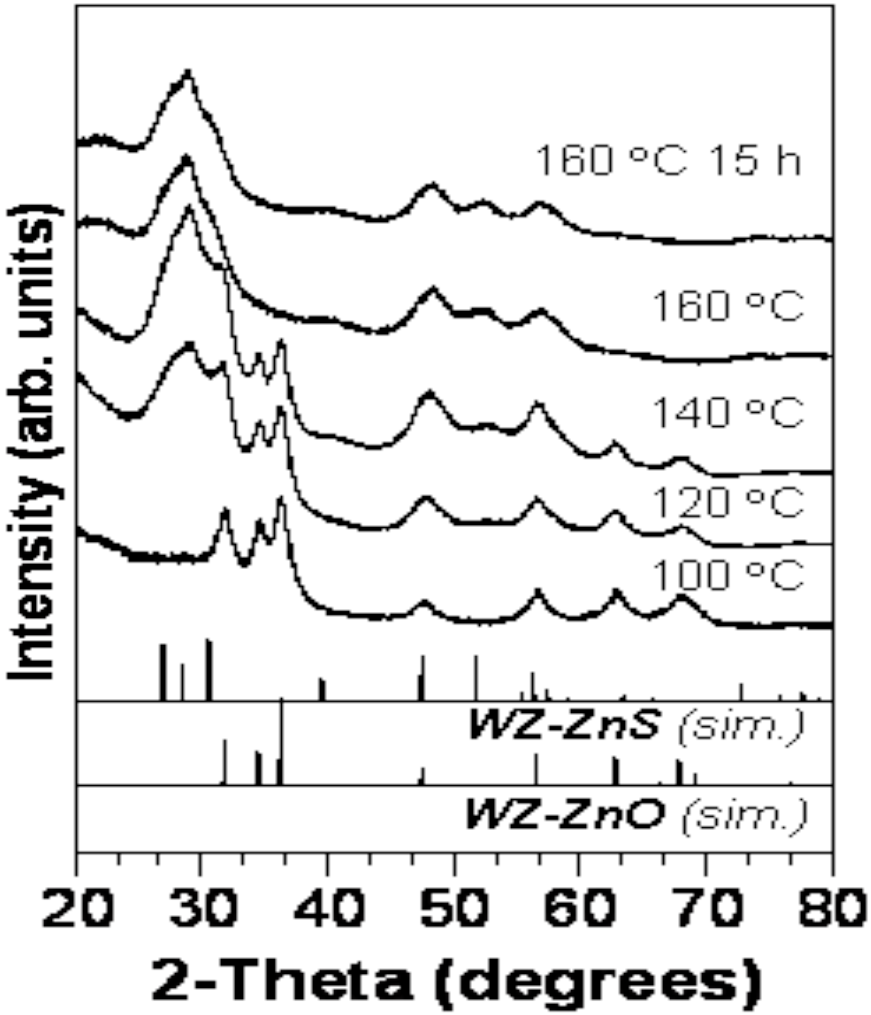
ABCABC

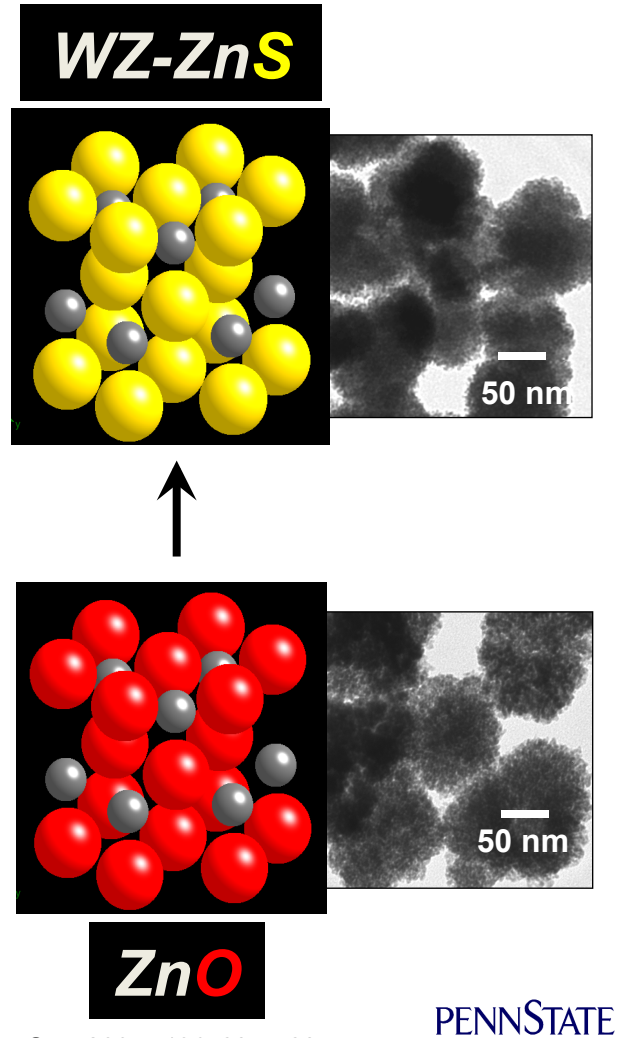
3.72 eV

Is it possible to control the formation of one over the other?

Abrikosov, N. K.; Bankina, V. F.; Poretskaya, L. V.; Shelimova, L. E.; Skudnova, E. V. Semiconducting II-VI, IV-VI, and V-VI Compounds; Plenum Press: New York, NY, 1969.

Synthesis of Wurtzite - ZnS

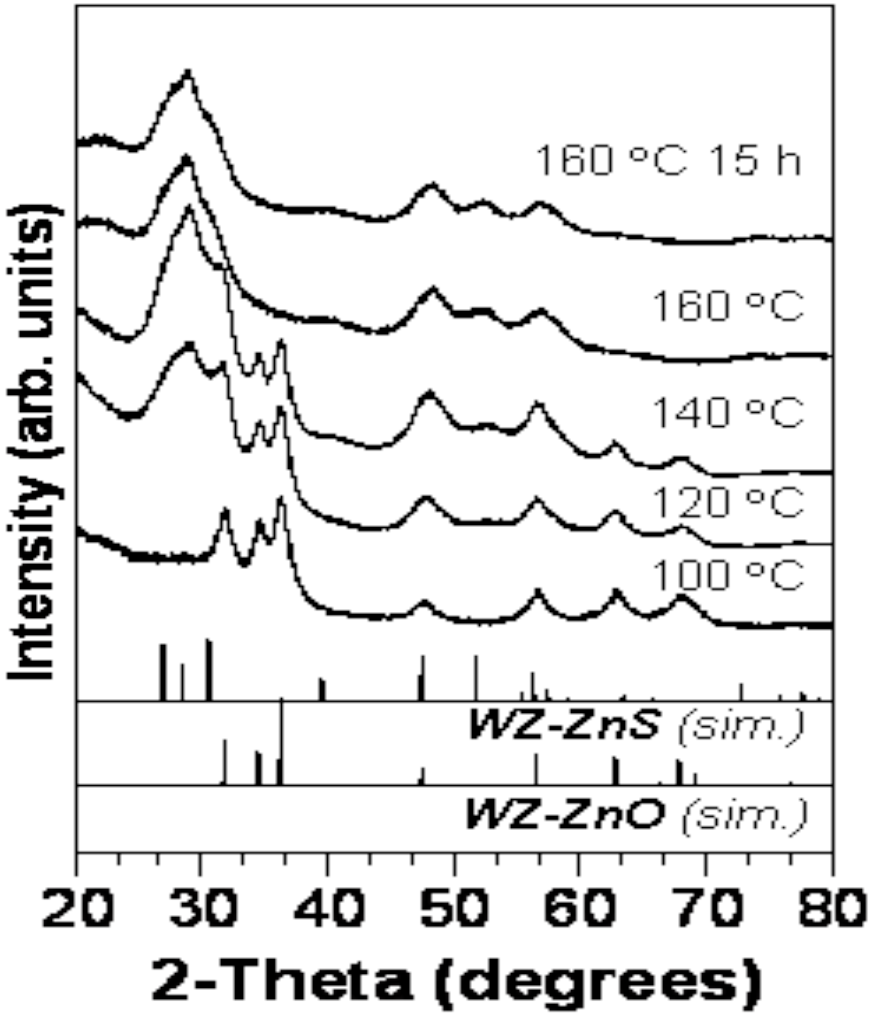


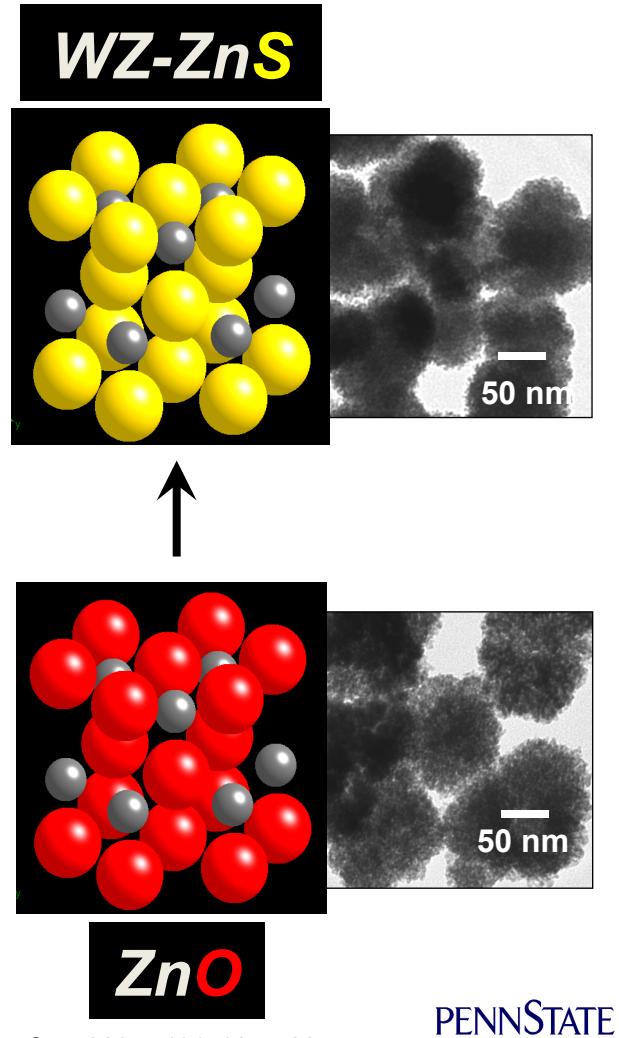


Zhao, Y.; Zhang, Y.; Zhu, H. Hadjipanayis, G. C.; Xiao, J. C. *J. Am. Chem. Soc.* **2004**, *126*, 6874-6875.
Dawood, F.; Schaak, R. E. *J. Am. Chem. Soc.* **2009**, *131*, 424-425.

Synthesis of Wurtzite - ZnS

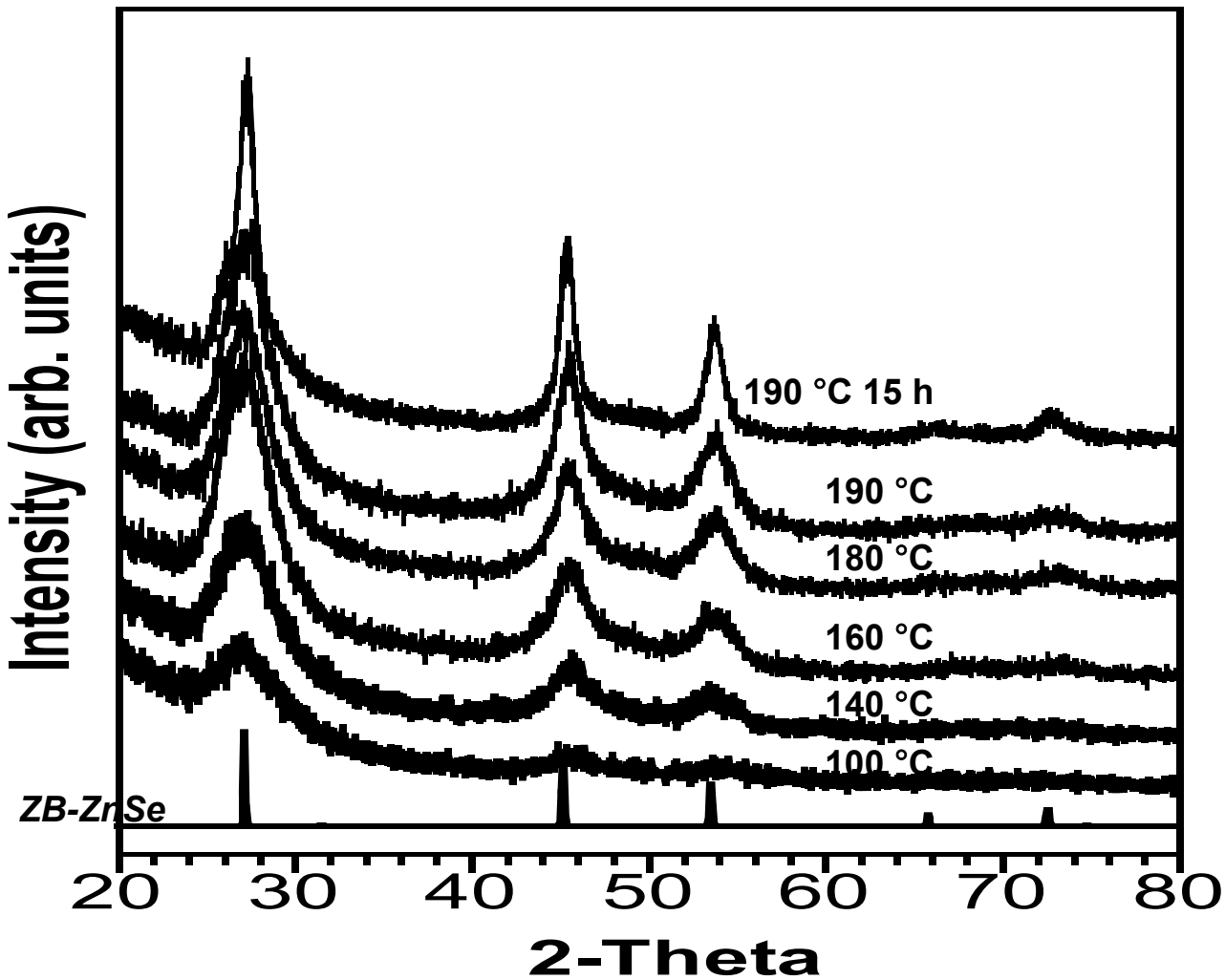
WZ ZnS forms when WZ ZnO is used as a reactive template





Zhao, Y.; Zhang, Y.; Zhu, H. Hadjipanayis, G. C.; Xiao, J. C. *J. Am. Chem. Soc.* **2004**, *126*, 6874-6875.
Dawood, F.; Schaak, R. E. *J. Am. Chem. Soc.* **2009**, *131*, 424-425.

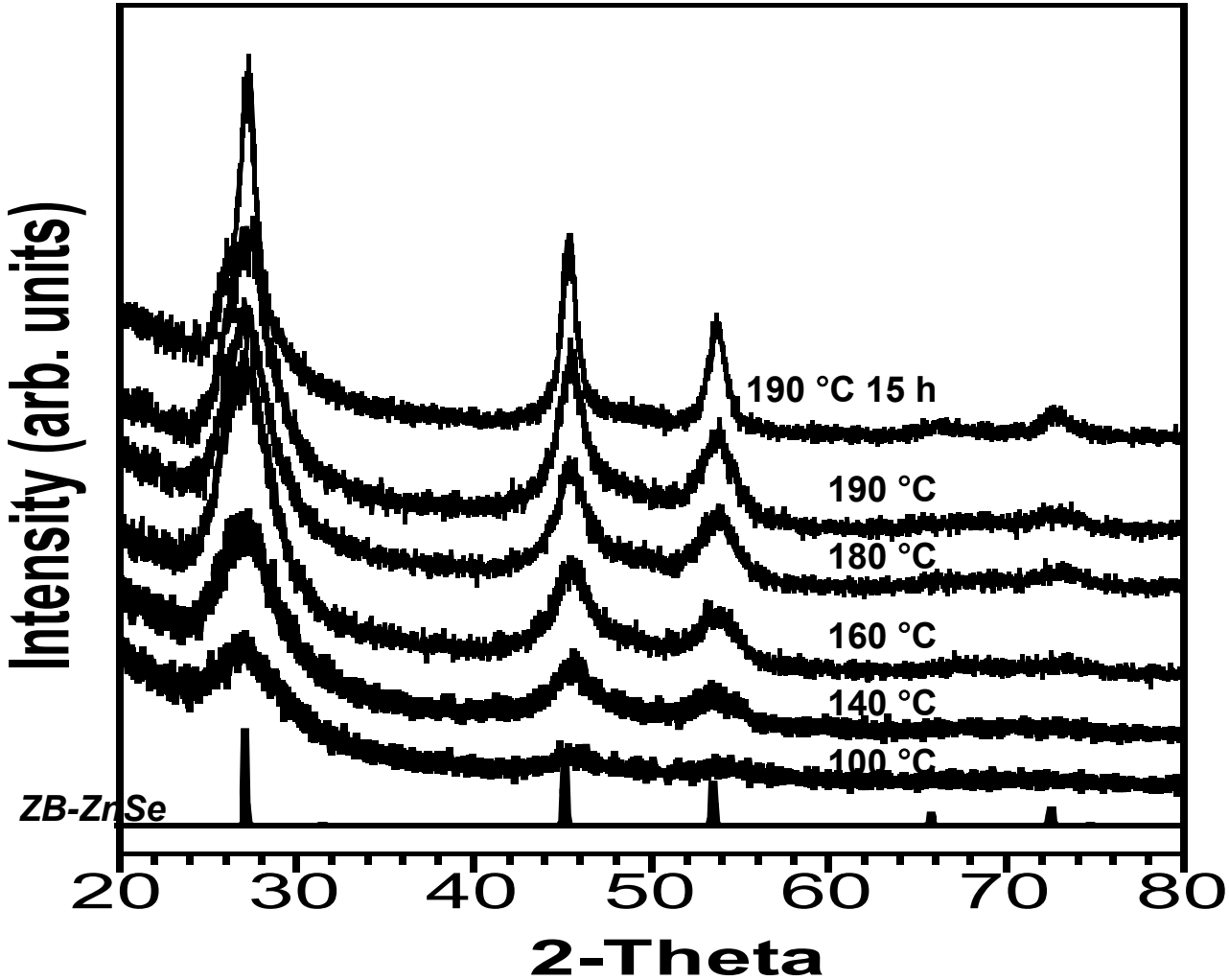
Control I: Prohibiting the Formation of ZnO



Dawood, F.; Schaak, R. E. *J. Am. Chem. Soc.* **2009**, *131*, 424-425.

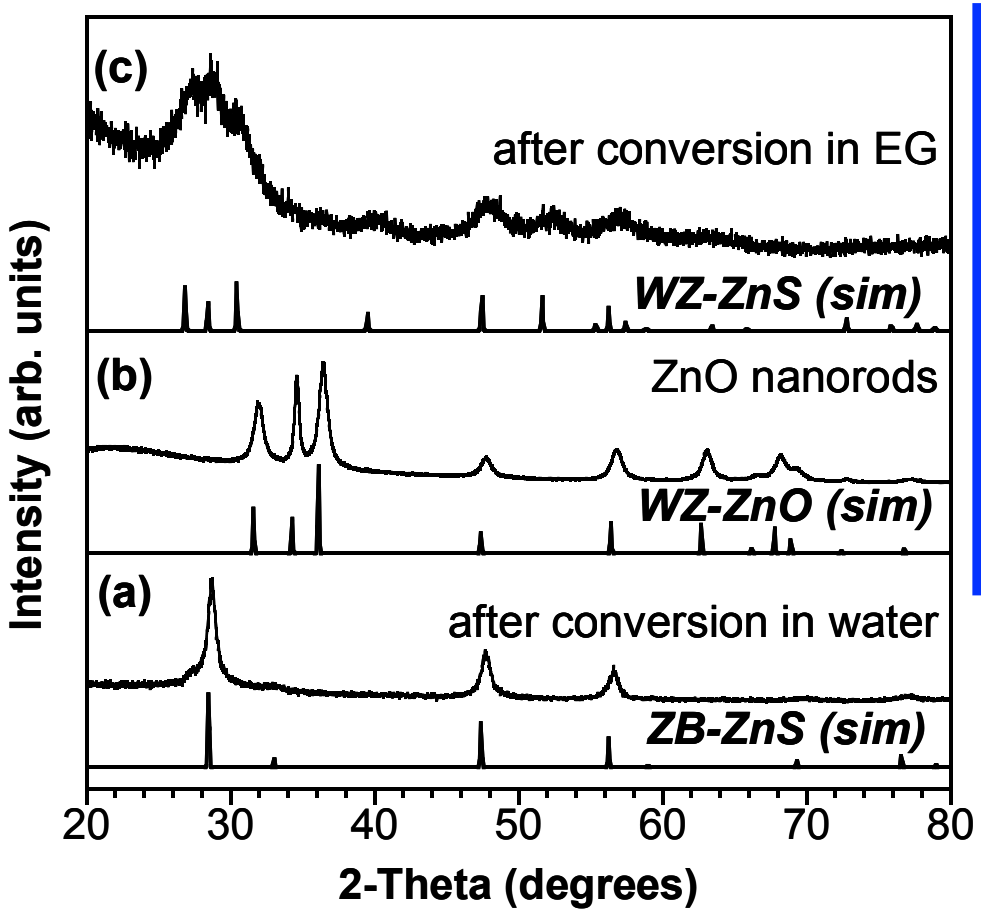
Control I: Prohibiting the Formation of ZnO

When WZ ZnO is not used as a reactive template, WZ ZnS does not form



Dawood, F.; Schaak, R. E. *J. Am. Chem. Soc.* **2009**, *131*, 424-425.

Control II: Ethylene Glycol vs. Water



Ethylene Glycol (EG)

Forms WZ-ZnS

Water

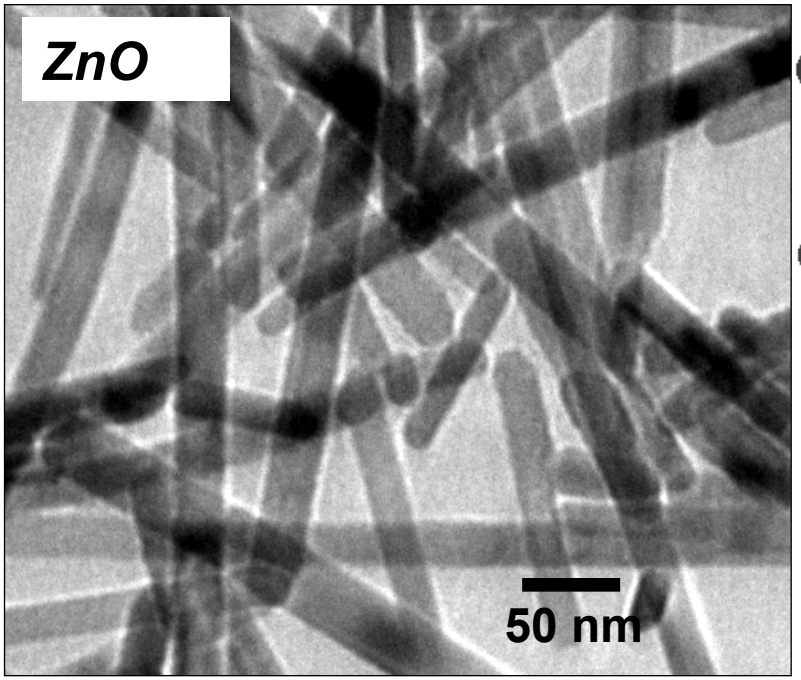
Forms ZB-ZnS

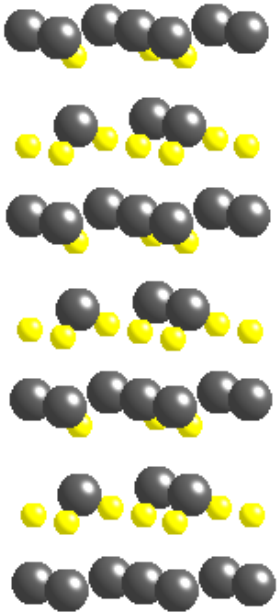
[ZnO dissolves in water (pH 9)]

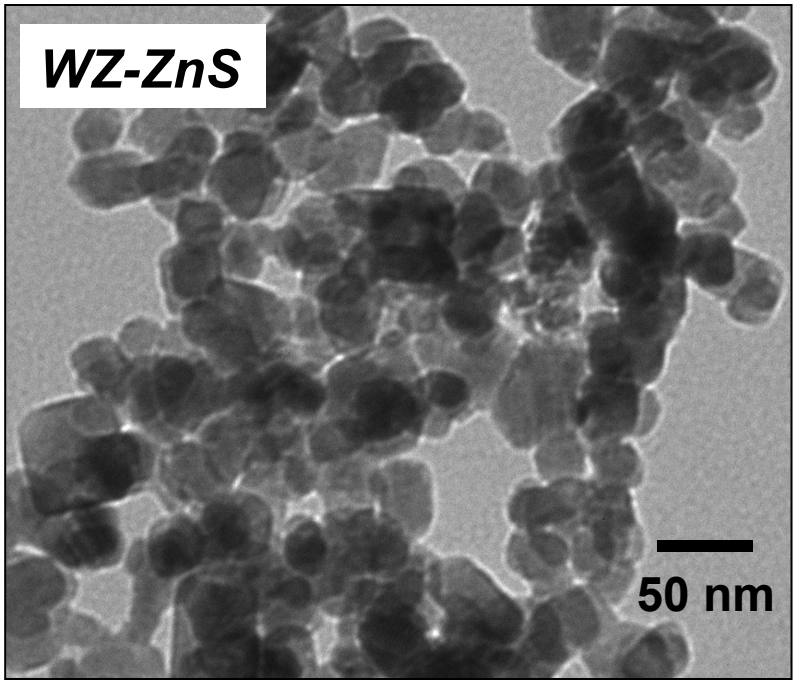
ZnO is stable in EG and acts as a structural template for the formation of WZ-ZnS

Dawood, F.; Schaak, R. E. *J. Am. Chem. Soc.* **2009**, *131*, 424-425.

Control III: Application to Pre-formed ZnO Nanorods







WZ-ZnS nanoparticles have diameter similar to diameter of ZnO nanorods

Consistent with ZnO nanorods breaking along length

Hints at atomic scale mechanism where oxygen is replaced by sulfur

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Dawood, F.; Schaak, R. E. *J. Am. Chem. Soc.* **2009**, *131*, 424-425.

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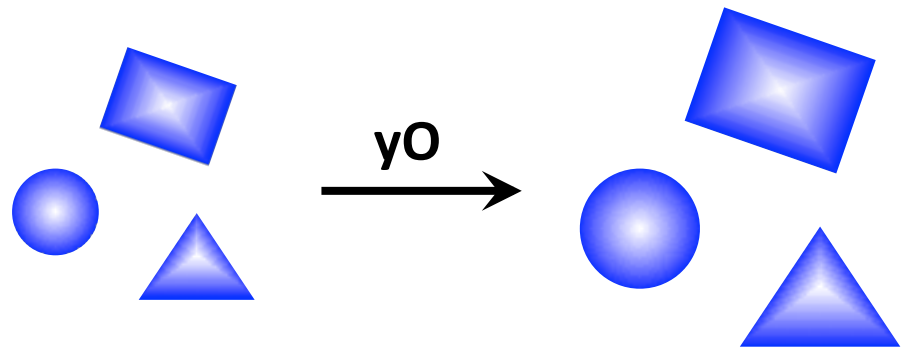
2. Compositional Templating



AB_x

binary intermetallic

Bi_2Pd , $BiPt$

AB_xO_y

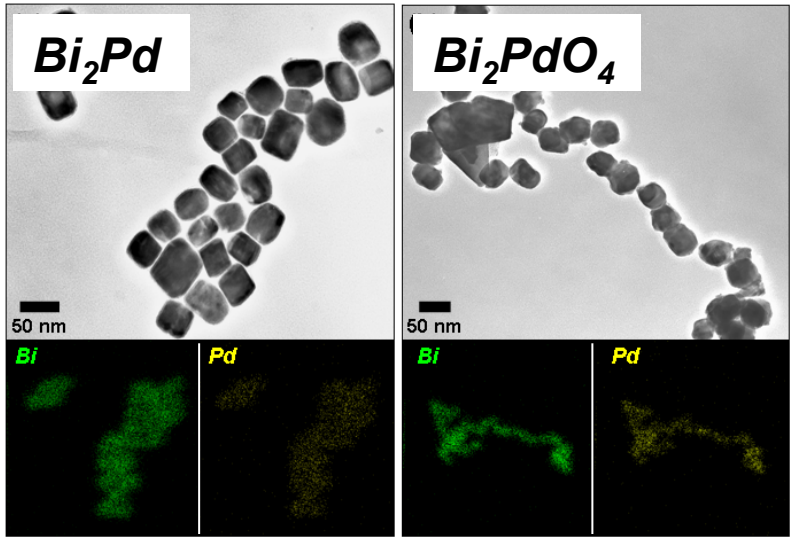
ternary oxide

Bi_2PdO_4 , $Bi_2Pt_2O_7$

Binary intermetallic nanoparticles as reactive precursors

Using a reactive template with a **narrow composition range** to further control the formation of the final product

Binary Intermetallics ⟶ Ternary Multimetal Oxides



$$Bi_2Pd \xrightarrow[O_2]{\Delta} Bi_2PdO_4$$

Bi_2Pd nanoparticles retain their cube-like morphology when oxidized to Bi_2PdO_4 at 780 °C.

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Dawood, F.; Leonard, B.M.; Schaak, R. E. *Chem. Mater.* **2007**, *19*, 4545-4550.

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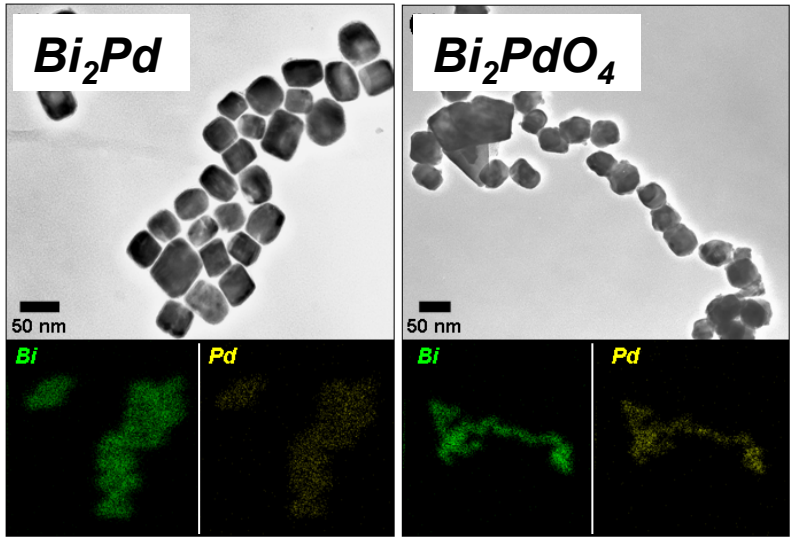
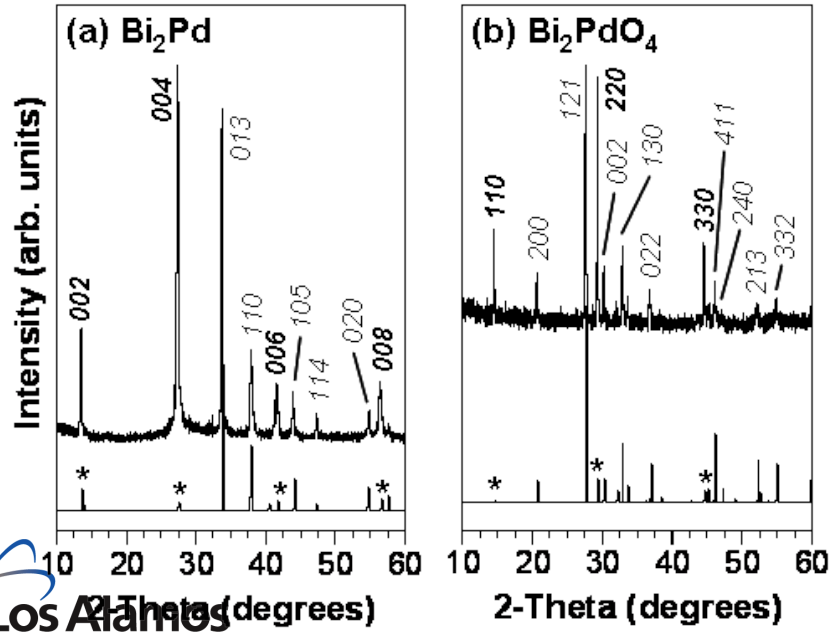
Binary Intermetallics ⟶ Ternary Multimetal Oxides





$$Bi_2Pd \xrightarrow[O_2]{\Delta} Bi_2PdO_4$$

Bi_2Pd nanoparticles retain their cube-like morphology when oxidized to Bi_2PdO_4 at 780 °C.

Select peaks show preferred orientation along the <001> direction for Bi_2Pd and <110> for Bi_2PdO_4.

Dawood, F.; Leonard, B.M.; Schaak, R. E. *Chem. Mater.* **2007**, *19*, 4545-4550.

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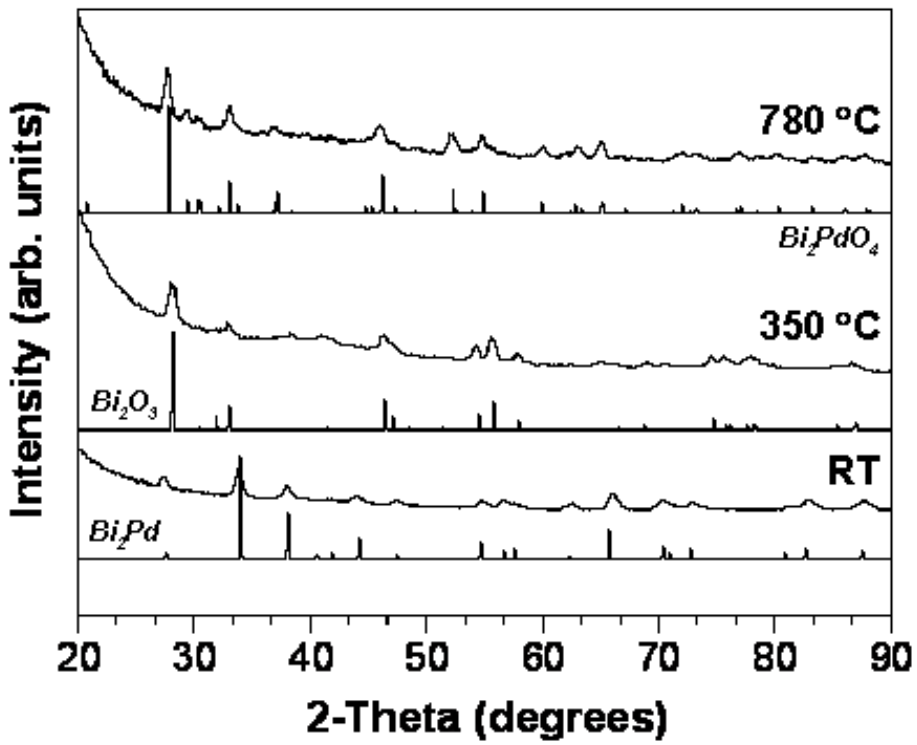
Probing the Reaction Pathway of Bi_2PdO_4 Formation

$$Bi_2Pd \xrightarrow[O_2]{\Delta} Bi_2O_3 / Pd \xrightarrow[O_2]{\Delta} Bi_2PdO_4$$



Starting material consists of only Bi_2Pd. Continued heating results in the formation of Bi_2PdO_4 at 780 °C.

Dawood, F.; Leonard, B.M.; Schaak, R. E. *Chem. Mater.* **2007**, *19*, 4545-4550.

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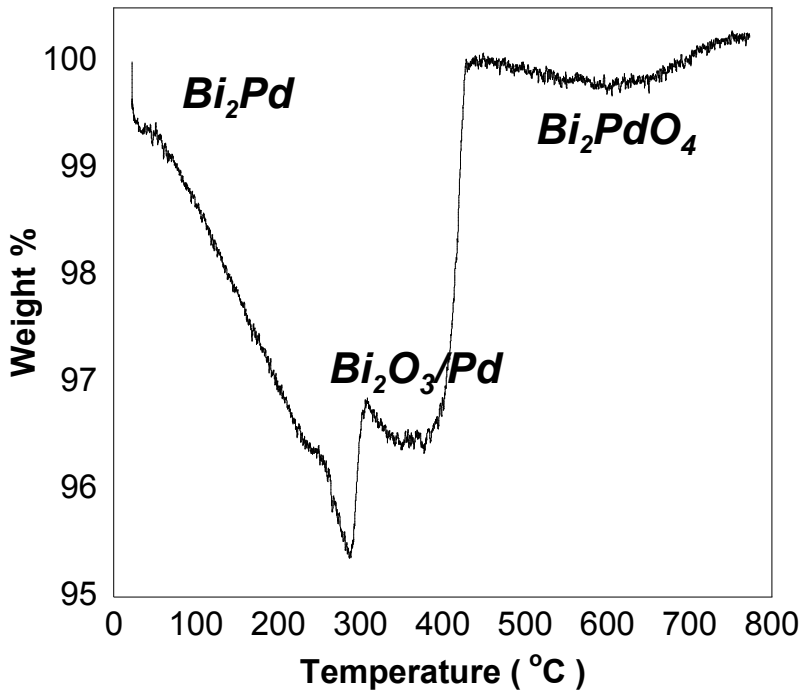

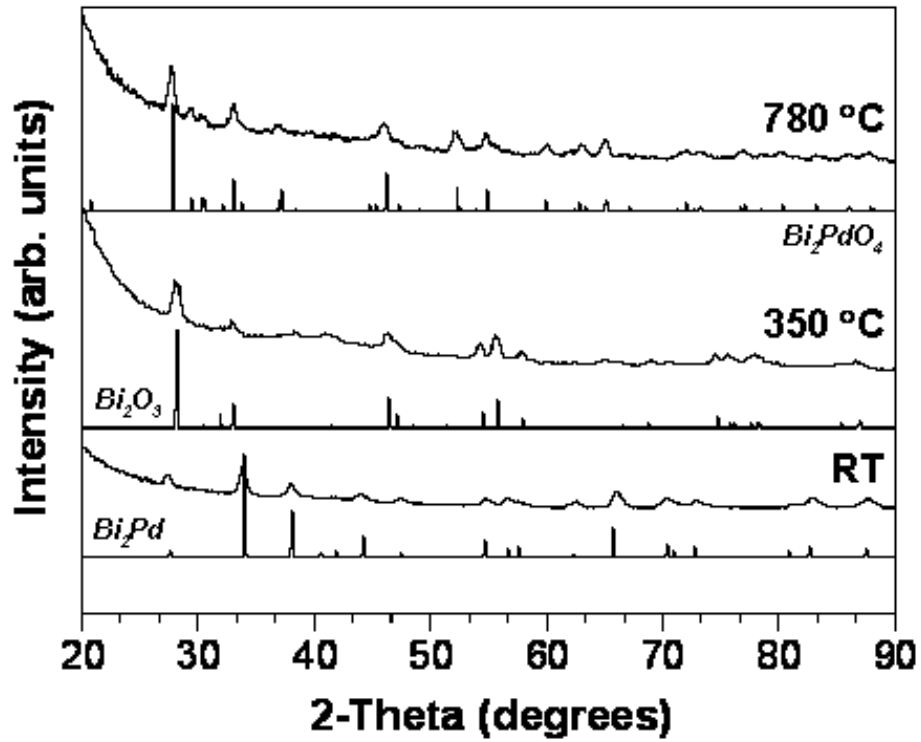

Representative weight change during oxidation of Bi_2Pd nanoparticles to form Bi_2PdO_4.

Starting material consists of only Bi_2Pd. Continued heating results in the formation of Bi_2PdO_4 at 780 °C.

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Dawood, F.; Leonard, B.M.; Schaak, R. E. *Chem. Mater.* **2007**, *19*, 4545-4550.

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Outline

Part I: Template-directed Colloidal Synthesis of Metastable Inorganic Nanoparticles

- Mechanism of Colloidal Synthesis
- Accessing Metastable Phases

Part II: Dip-Pen Nanolithography of Colloidal Nanoparticles on Sub-micron Surfaces

- Semiconductor Nanoparticles
- Dip-pen Nanolithography

Lithography

the process of printing/drawing on a surface

http://www.appleturnover.tv/mt/mt-search.cgi?IncludeBlogs=9&tag=fountain%20pen&limit=20

Lithography

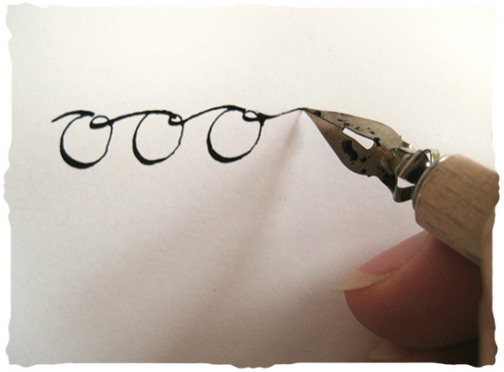
the process of printing/drawing on a surface

Calligraphy

fountain pen and ink

step 1: inking pen

inked pen



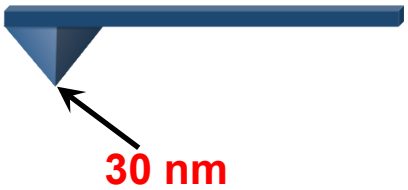
step 2: writing

is it possible to perform calligraphy on the nanoscale?

http://www.appleturnover.tv/mt/mt-search.cgi?IncludeBlogs=9&tag=fountain%20pen&limit=20

Dip-Pen Nanolithography

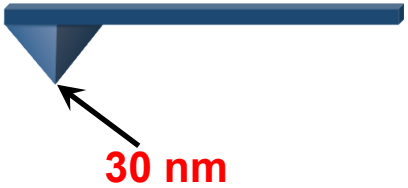
uses an “ink” coated AFM tip to create patterns on a surface



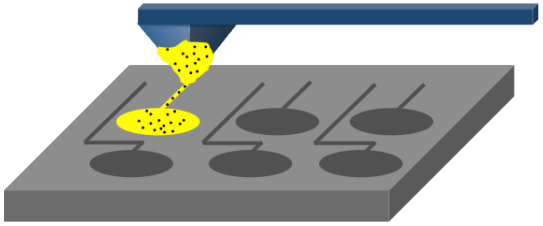
atomic force microscopy (AFM) tip

Dip-Pen Nanolithography (DPN)

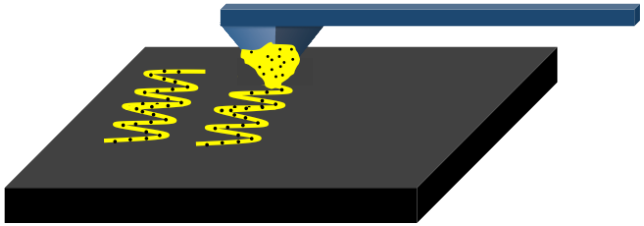
uses an “ink” coated AFM tip to create patterns on a surface



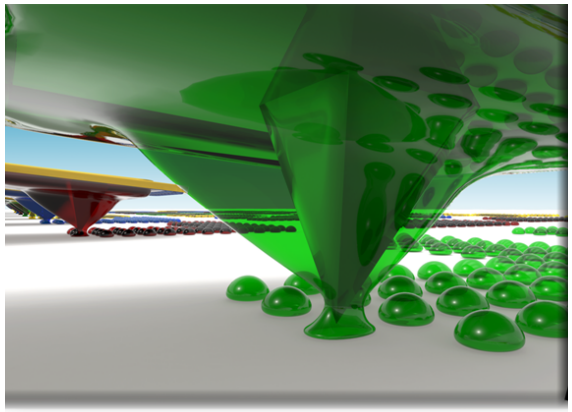
atomic force microscopy (AFM) tip



step 1: inking AFM tip



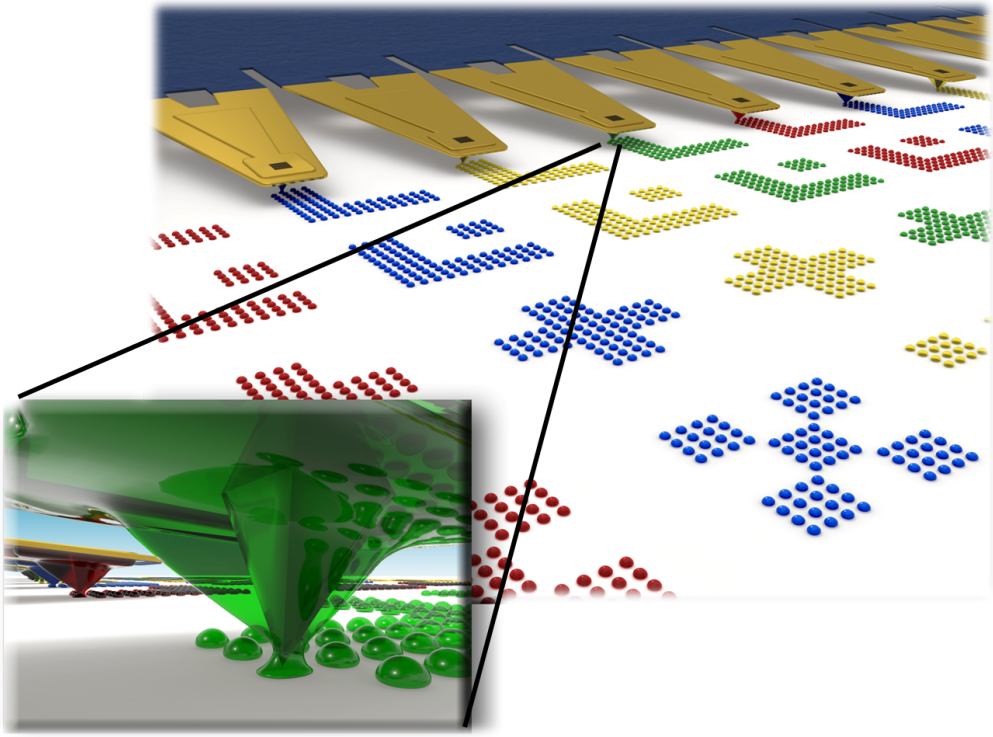
step 2: writing with AFM tip



patterning multiple spots on a substrate with DPN

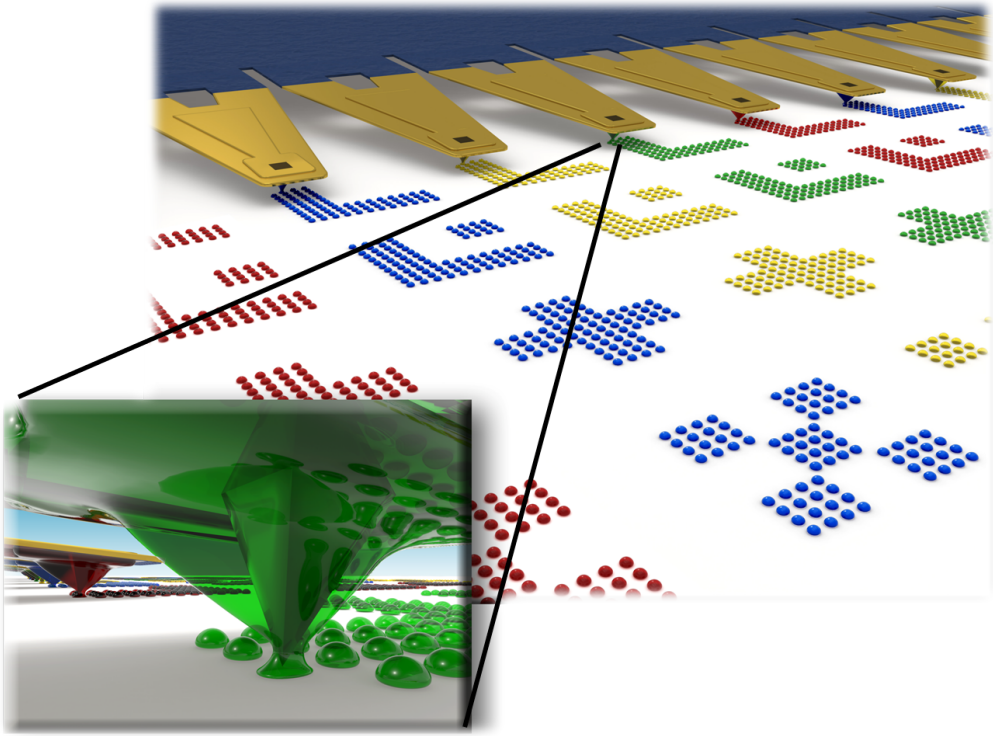
Mirkin et al. Nat. Nanotechnol. **2007**, 2, 145.

Dip-Pen Nanolithography – Controlling Surface Structuring on the Nanometer Scale



Mirkin et al. Angew. Chemie. **2004**, 2, 30.

Dip-Pen Nanolithography – Controlling Surface Structuring on the Nanometer Scale

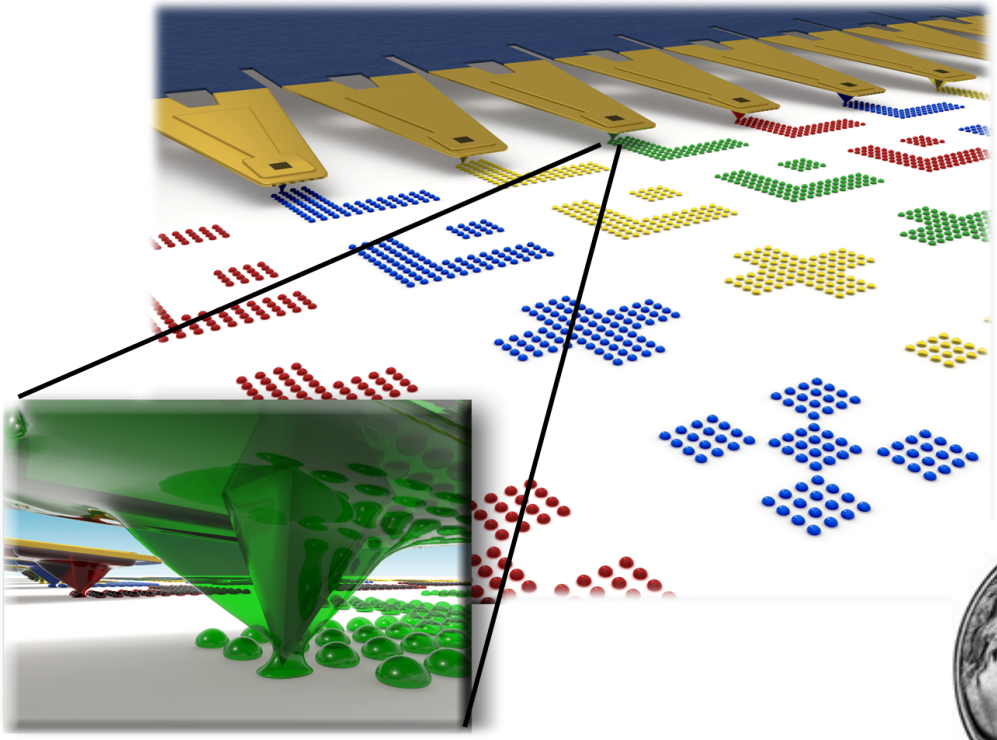


works with "inks" that are in the liquid state

small organic molecules, proteins, DNA, peptides, polymers, colloidal nanoparticles

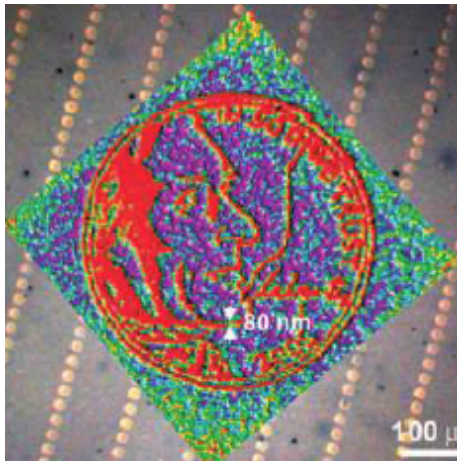
Mirkin et al. Angew. Chemie. **2004**, 2, 30.

Dip-Pen Nanolithography – Controlling Surface Structuring on the Nanometer Scale



works with "inks" that are in the liquid state

immunoglobulin G patterned on glass



organic molecules patterned on gold

small organic molecules, proteins, DNA, peptides, polymers, colloidal nanoparticles

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Mirkin et al. Angew. Chemie. **2004**, 2, 30.

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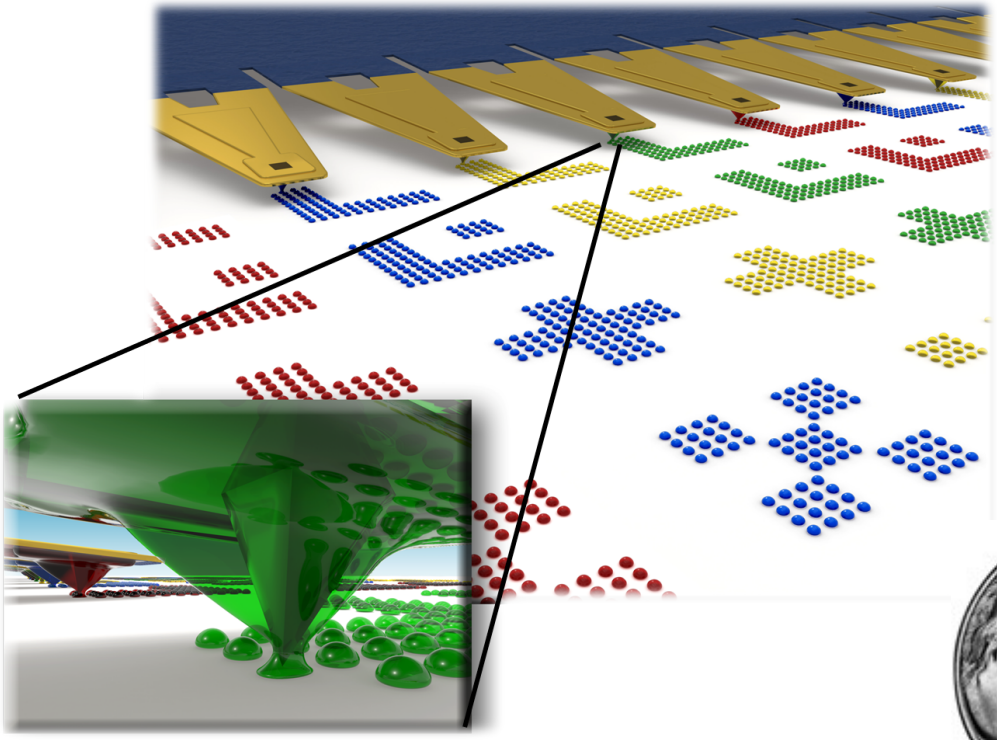
Dip-Pen Nanolithography – Controlling Surface Structuring on the Nanometer Scale



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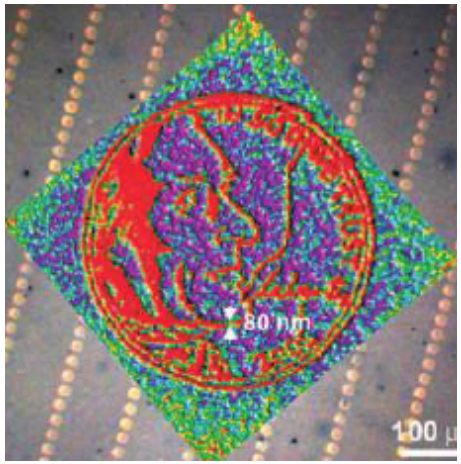


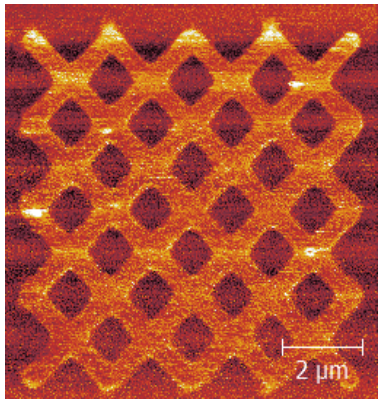
organic molecules patterned on gold

small organic molecules, proteins, DNA, peptides, polymers, colloidal nanoparticles

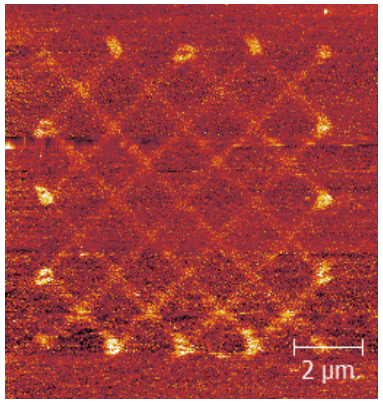
compatible with many surfaces

Mirkin et al. Angew. Chemie. **2004**, 2, 30.

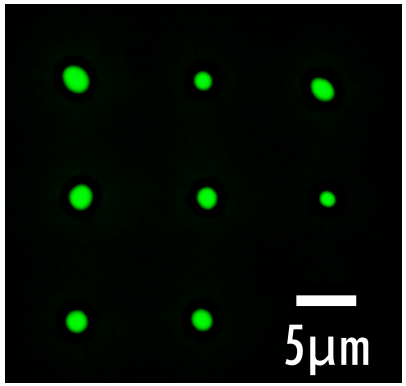
Dip-Pen Nanolithography at CINT



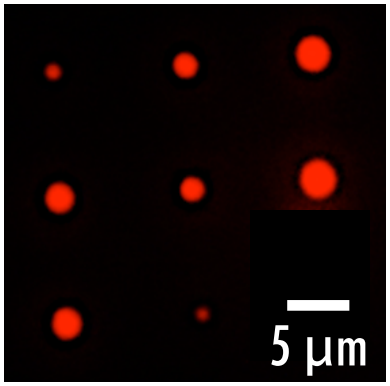
low speed



high speed



silicon

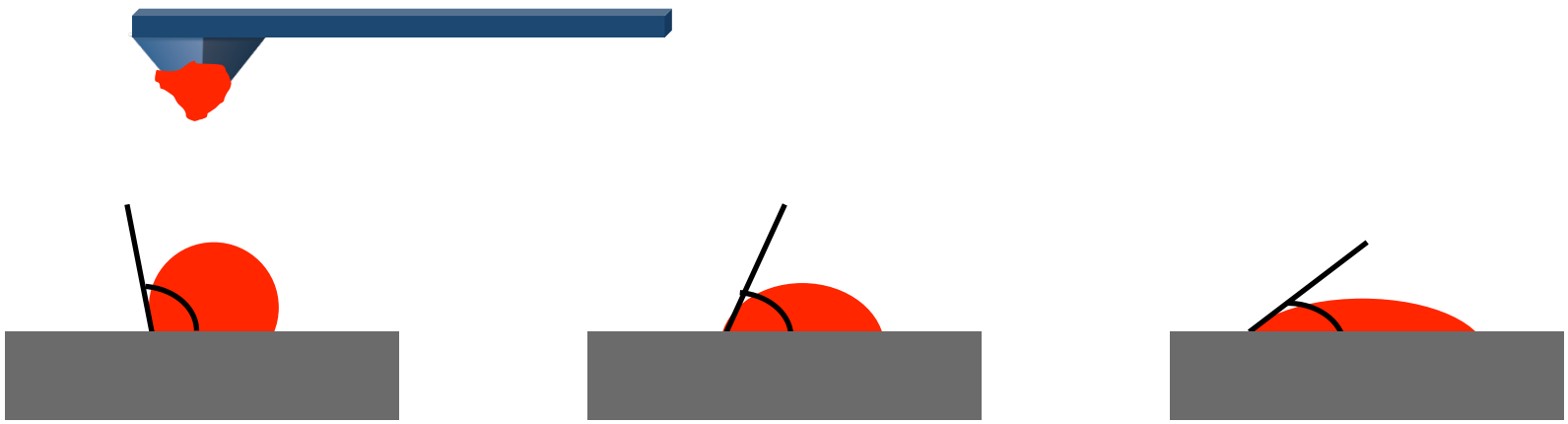


polymer

16-mercaptohexadecanoic acid patterned on gold

fluorescent semiconductor nanoparticles patterned

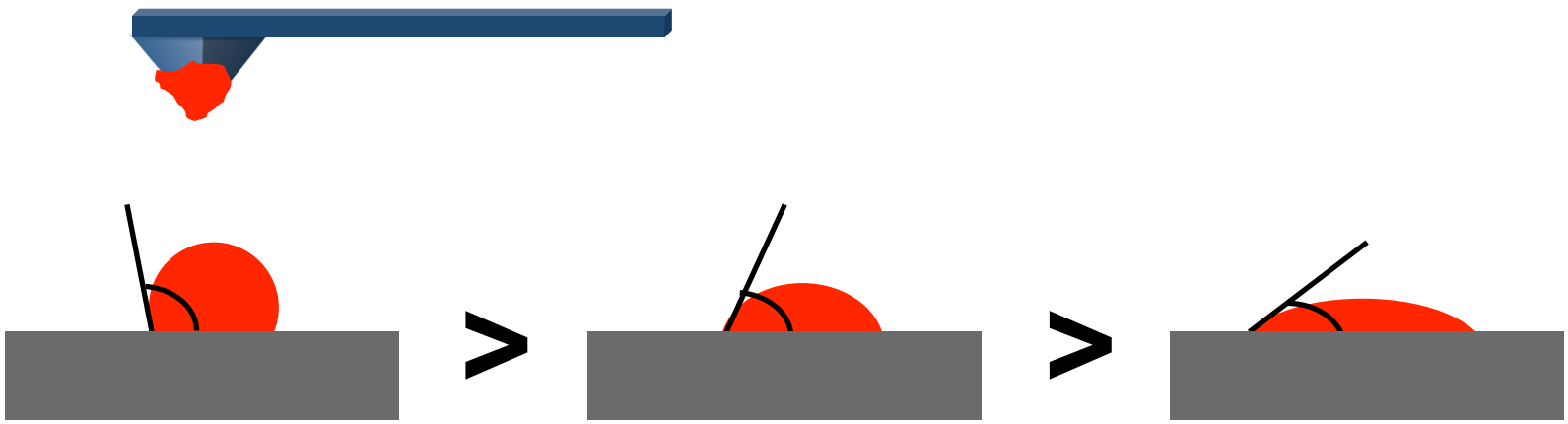
Interaction of Liquids with Solid Surfaces



contact angle

measurement of “wettability”

Interaction of Liquids with Solid Surfaces



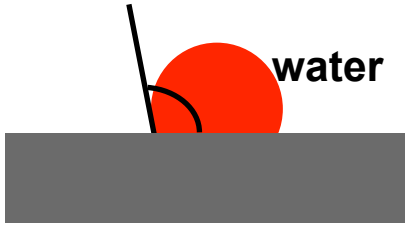
contact angle

measurement of “wettability”

Interaction of Liquids with Solid Surfaces

contact angle

measurement of "wettability"



waxed surface of car

Hydrogen-bonds and dipole-dipole interactions in water **>>>** **VdW forces in wax**

http://s11.photobucket.com/user/the01cav/media/IMG_4390.jpg.html

http://www.sheinside.com/Yellow-Vintage-Dot-Raincoat-Outerwear-p-84467-cat-1735.html

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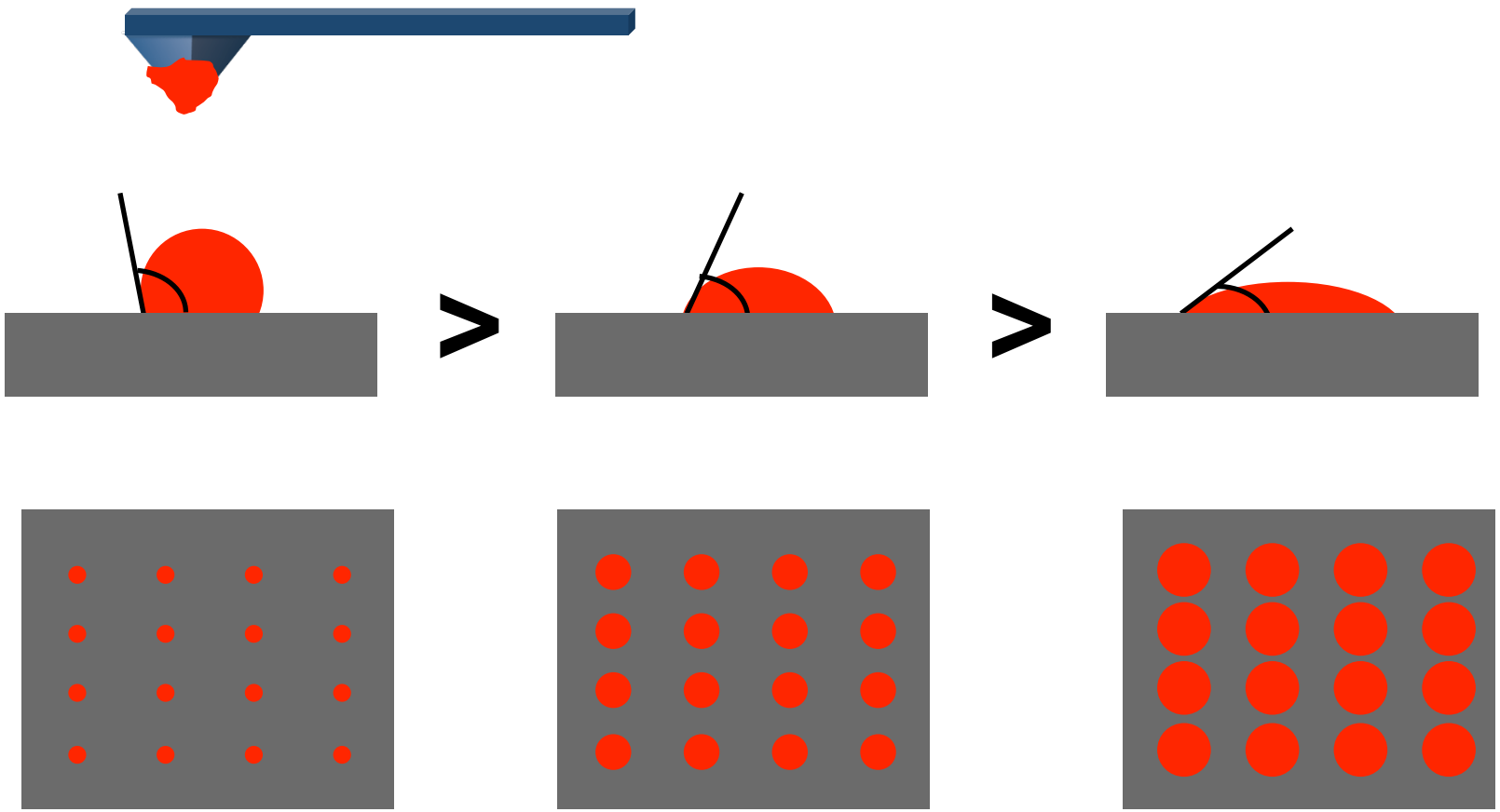
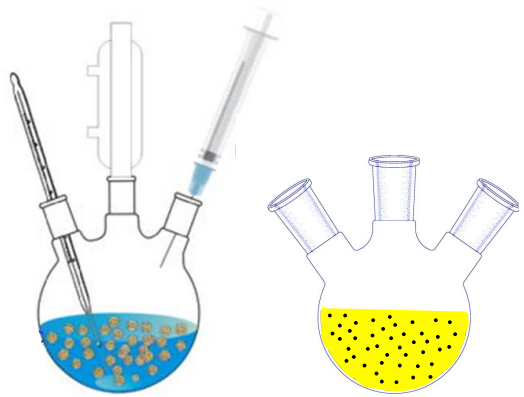
Contact Angle for DPN



contact angle determines spot size of patterned liquid

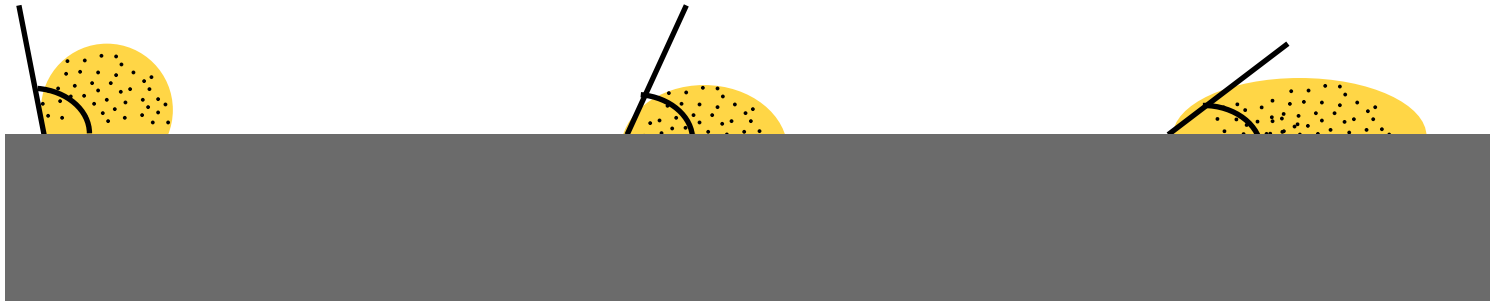
Patterning Nanoparticles on Nanometer-sized Surfaces

DPN works with "inks" that are in the liquid state

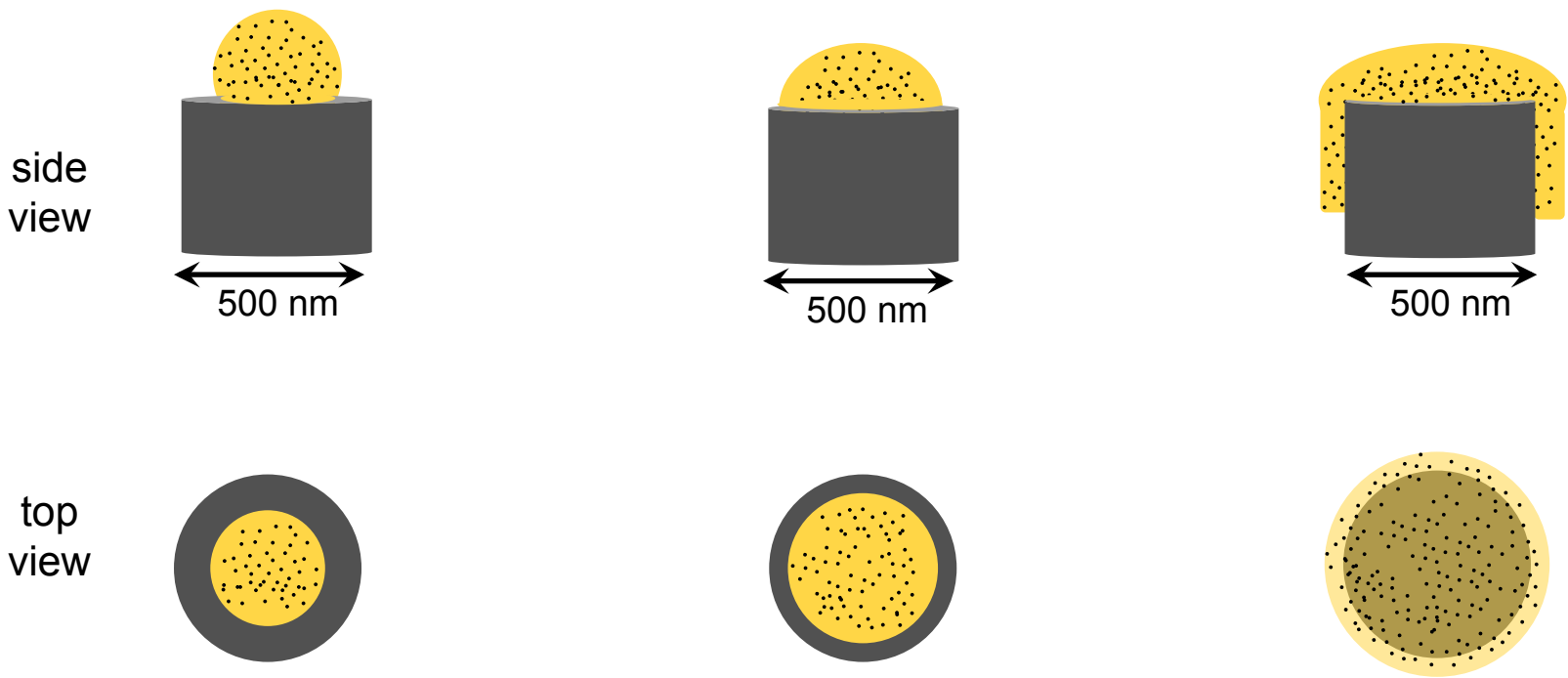


semiconductor nanoparticles in solution

Patterning Nanoparticles on Nanometer-sized Surfaces

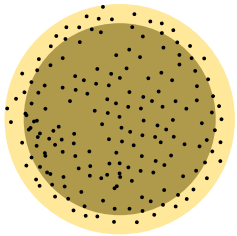


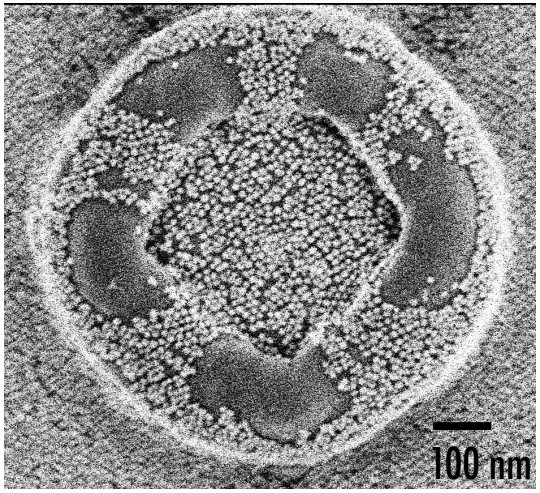
Patterning Nanoparticles on Nanometer-sized Pillars



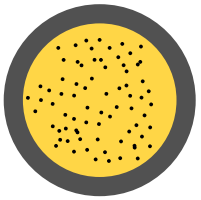
contact angle is important for patterning a liquid especially when the surface area decreases

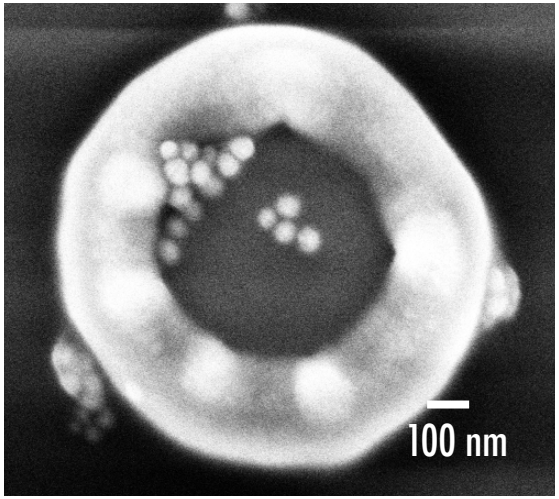
Patterning Semiconductor Nanoparticles (in solution) on Silicon Nanopillars



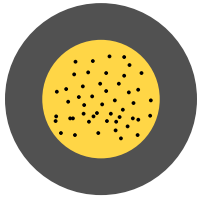


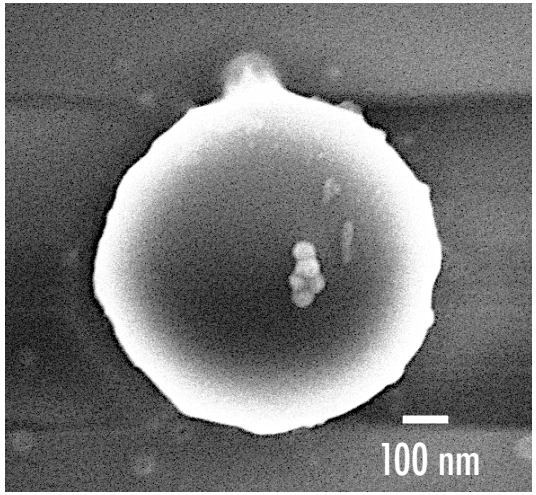
contact angle: <10°





contact angle: 28°





contact angle: 35°

SEM images collected by Chris Sheehan- CINT,LANL

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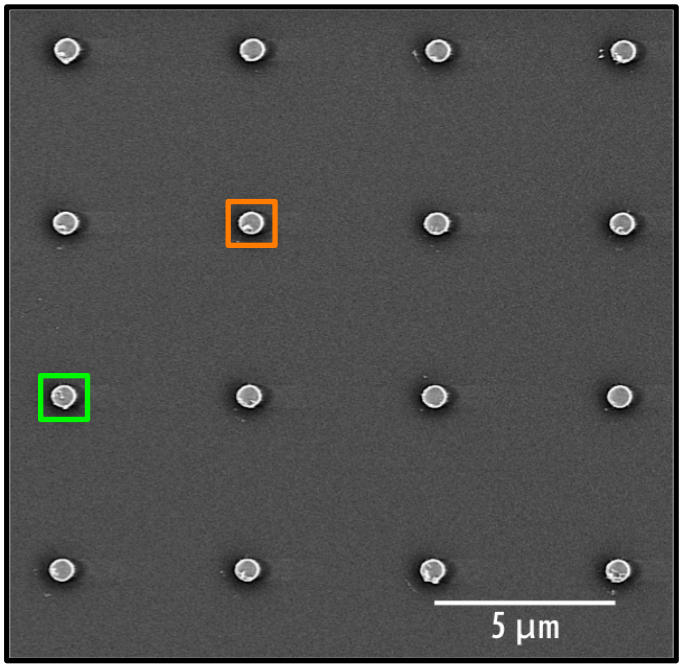
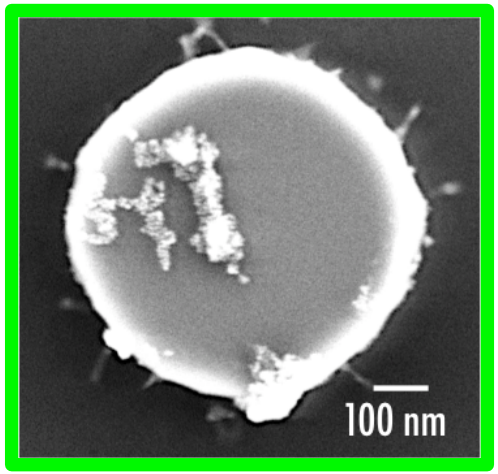
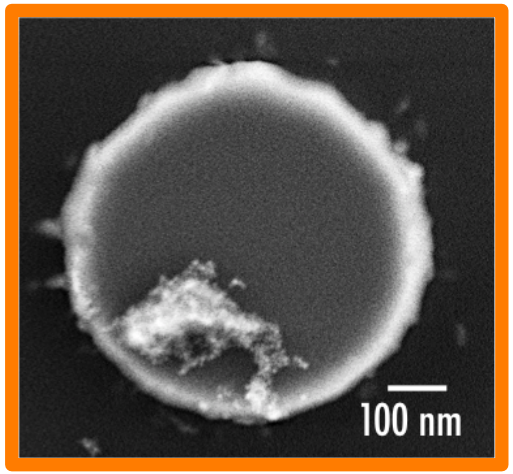
Placement of Nanoparticles on Silicon Nanopillars

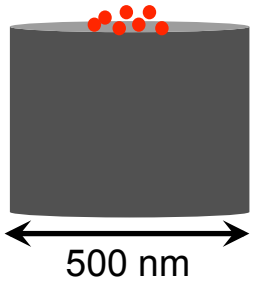


semiconductor nanoparticles patterned on 16 silicon nanopillars





individual silicon nanopillars where semiconductor nanoparticles have been placed on top



when fluorescent semiconductor nanoparticles are placed only on top of silicon nanopillars, the pillars can direct the fluorescence

SEM images collected by Chris Sheehan- CINT,LANL

Proposed Research

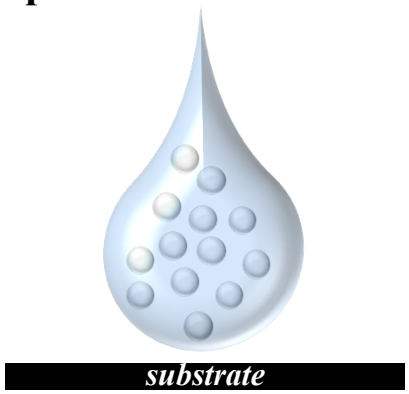
Nanosphere Lithography: A Versatile Tool for Patterning Materials

Nanosphere Lithography (NSL)

Based on the formation of a close-packed monolayer of uniform silica or polymer nanospheres, forming a “mask”

Inexpensive, solution based, substrate general

Step 1: Drop coating nanosphere suspension onto substrate

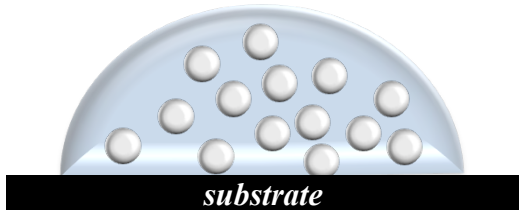


Nanosphere Lithography (NSL)

Based on the formation of a close-packed monolayer of uniform silica or polymer nanospheres, forming a “mask”

Inexpensive, solution based, substrate general

Step 2: Evaporation of solvent

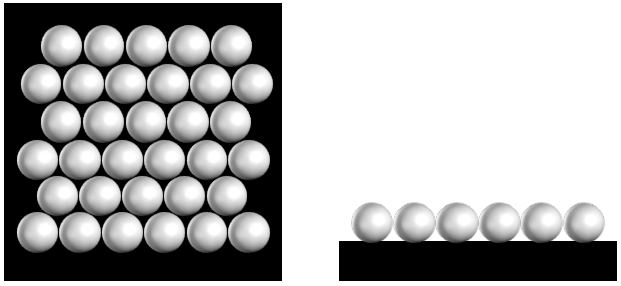


Nanosphere Lithography (NSL)

Based on the formation of a close-packed monolayer of uniform silica or polymer nanospheres, forming a “mask”

Inexpensive, solution based, substrate general

Step 3: *hcp* arrangement of nanospheres



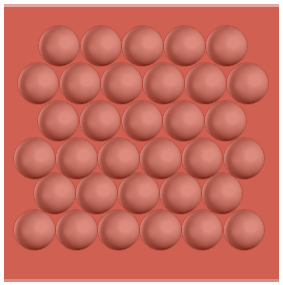
top view ***side view***

Nanosphere Lithography (NSL)

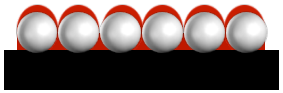
Based on the formation of a close-packed monolayer of uniform silica or polymer nanospheres, forming a “mask”

Inexpensive, solution based, substrate general

Step 4: Deposition of desired material



top view



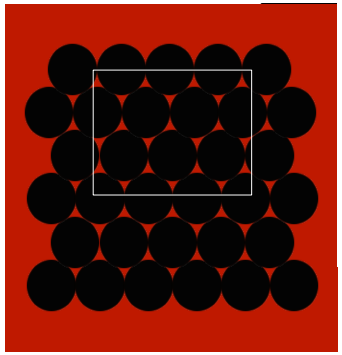
side view

Nanosphere Lithography (NSL)

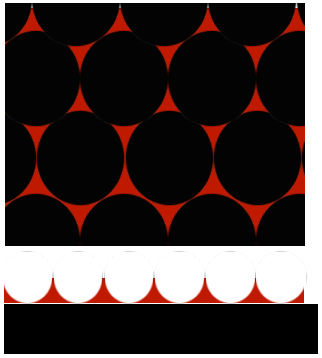
based on the formation of a close-packed monolayer of uniform silica or polymer nanospheres, forming a “mask”

inexpensive, solution based, substrate general

Step 5: Removal of nanosphere mask



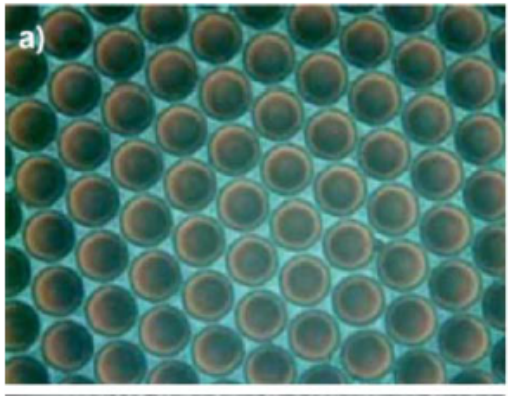
top view



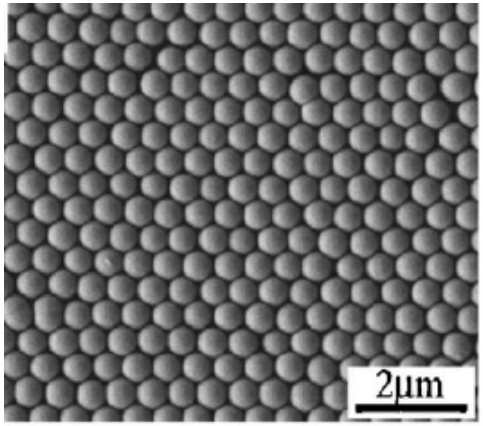
side view

patterned areas (red)

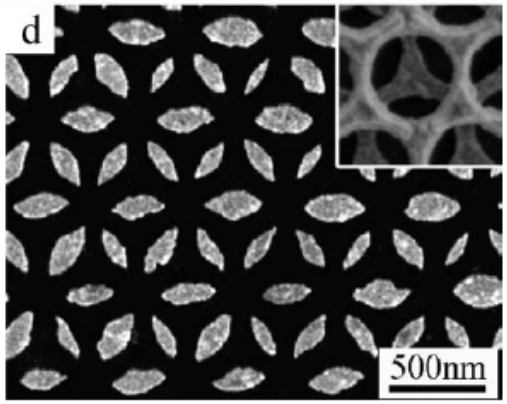
Versatility of Nanosphere Lithography



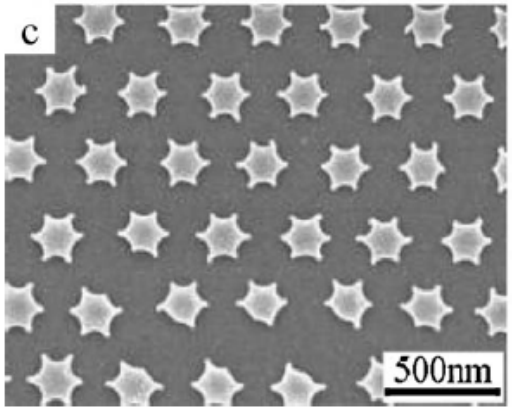
glass nanospheres
(artificial mosquito eye)



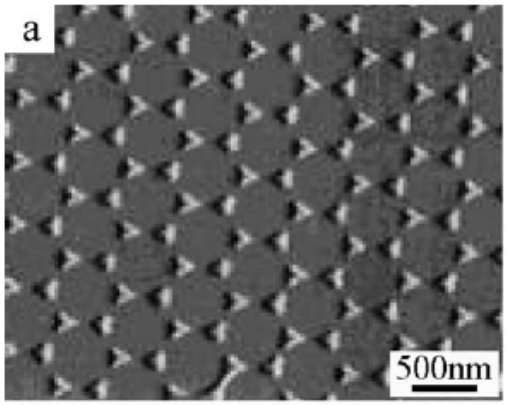
NSL mask



gold nanopatterns



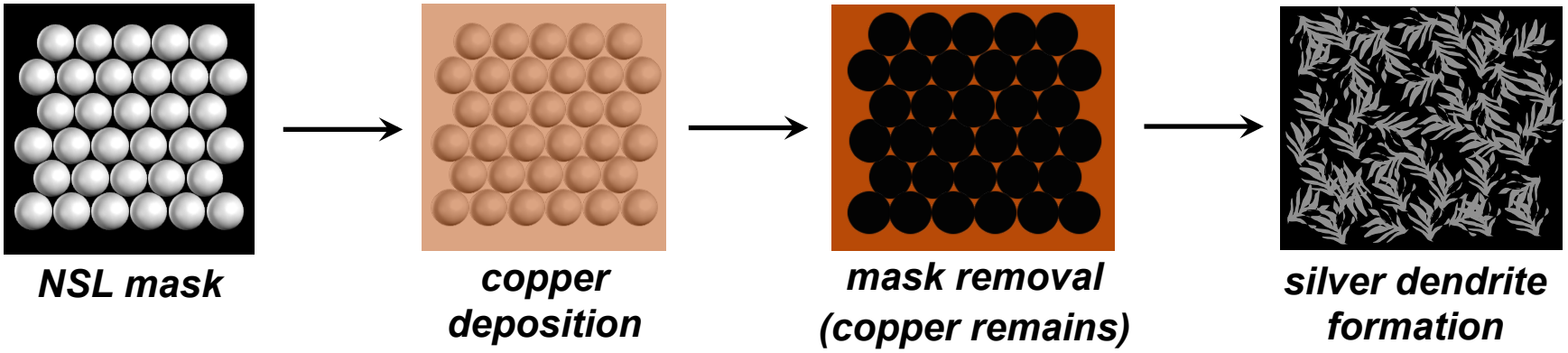
polymer nanostars



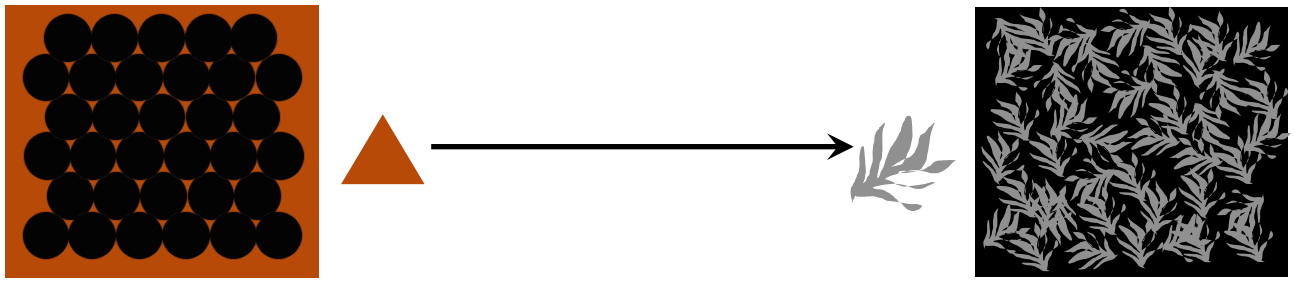
silver nanotriangles

Qi, L.; Ye, X. *Nano Today* **2011**, *6*, 608.

Project 1: Growth of large area, two-dimensional nanostructured surfaces



Step 1: Formation of Silver Dendritic Nanostructures



mask removal (copper remains)

silver dendrite formation

$$Cu_{(s)} \longrightarrow Cu^{2+}_{(aq)} + 2\,e$$

$$Ag^{+}_{(aq)} + e \longrightarrow Ag_{(s)}$$

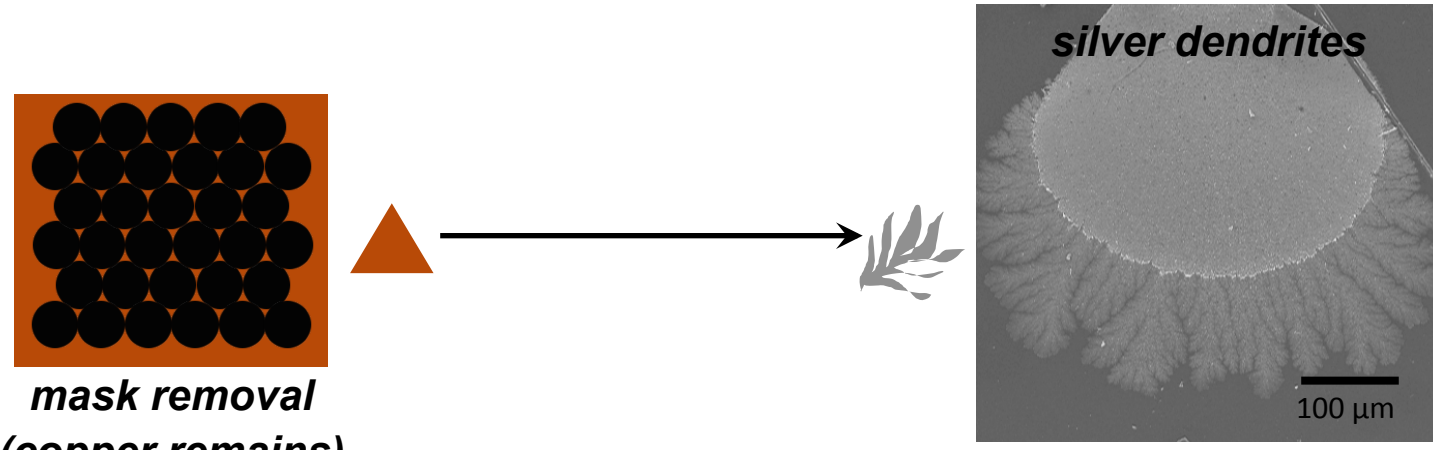
$$Cu_{(s)} \longrightarrow Cu^{2+}_{(aq)} + 2\,e \qquad E° - 0.34\ V$$

$$Ag^{+}_{(aq)} + e \longrightarrow Ag_{(s)} \qquad E° + 0.80\ V$$

$$Cu_{(s)} + 2Ag^{+}_{(aq)} \longrightarrow 2Ag_{(s)} + Cu^{2+}_{(aq)} \qquad E° + 0.46\ V$$

favorable reaction

Step 1: Formation of Silver Dendritic Nanostructures



mask removal (copper remains)

$$Cu_{(s)} \longrightarrow Cu^{2+}_{(aq)} + 2\,e$$

$$Ag^{+}_{(aq)} + e \longrightarrow Ag_{(s)}$$

$$Cu_{(s)} \longrightarrow Cu^{2+}_{(aq)} + 2\,e \qquad E° - 0.34\ V$$

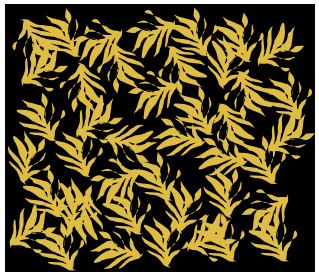
$$Ag^{+}_{(aq)} + e \longrightarrow Ag_{(s)} \qquad E° + 0.80\ V$$

$$Cu_{(s)} + 2Ag^{+}_{(aq)} \longrightarrow 2Ag_{(s)} + Cu^{2+}_{(aq)} \qquad E° + 0.46\ V$$

favorable reaction

Step 2: Template Based Conversion to Form Ag_2S

silver dendrites

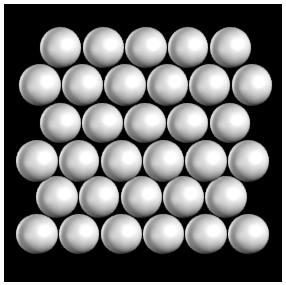


Ag_2S formation

$$2Ag_{(s)} + S \longrightarrow Ag_2S_{(s)}$$

Large areas of nanostructured materials are useful for catalysis

Project 2: Microtransfer Molding for Spatial Organization of Colloidal Nanocatalysts

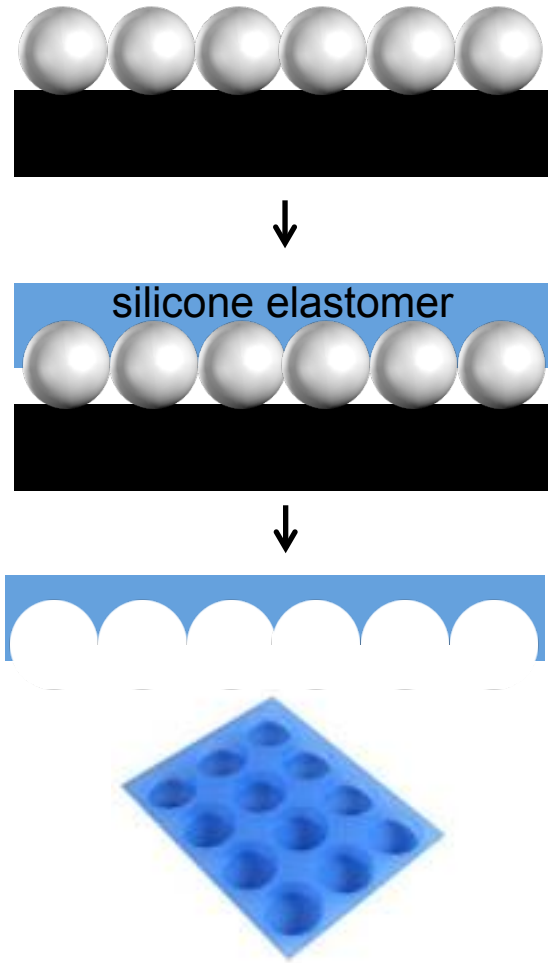


NSL mask

Is it possible to place pre-made nanoparticles in the void spaces?

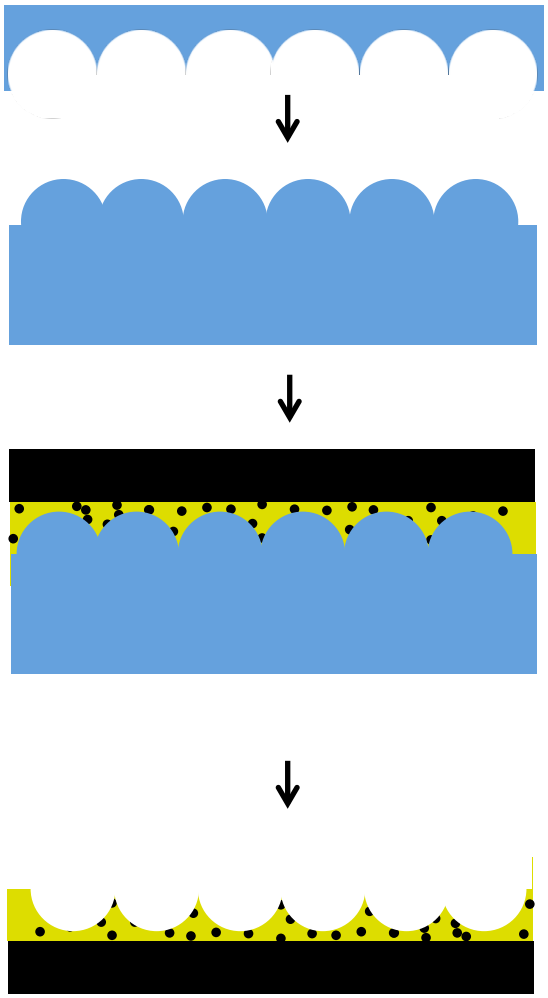
How can nanospheres be removed without removing nanoparticles?

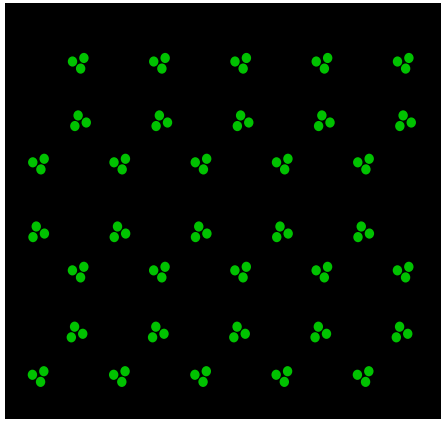
Need a replica of the nanospheres!



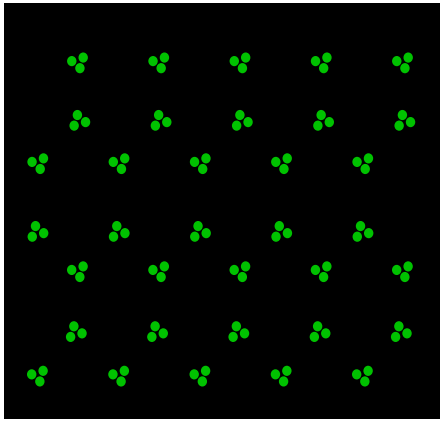
silicone baking mold

Project 2: Microtransfer Molding for Spatial Organization of Colloidal Nanocatalysts

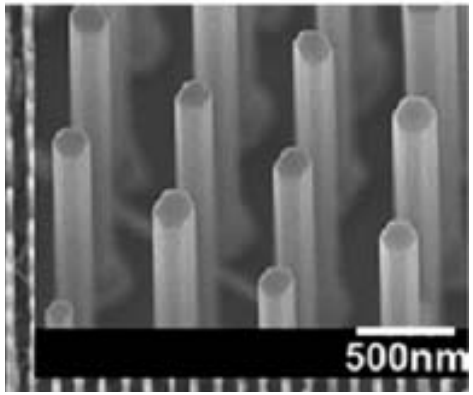




Project 2: Microtransfer Molding for Spatial Organization of Colloidal Nanocatalysts



catalyst nanoparticles



catalyzed growth of ordered nanowires

Conclusions

- Template directed synthesis is a powerful approach for synthesis of complex nanocrystalline inorganic solids
- Compositional, Morphological, and Structural templating have been demonstrated of nanocrystals have been demonstrated for the predictable synthesis of metastable materials
- New templating mechanisms such as structural templating could lead to the formation of new materials

Acknowledgements

Prof. Raymond E. Schaak

Prof. John T. Fourkas

Dr. Jennifer Hollingsworth

Schaak group members

Fourkas group members

Hollingsworth group members

Prof. Stanton Ching

Faculty at Connecticut College

Huck Institute of Life Sciences, The Pennsylvania State University

Maryland Nanocenter, University of Maryland

Center for Integrated Nanotechnologies, Los Alamos National Laboratory

Los Alamos NATIONAL LABORATORY EST. 1943

LA-UR

U.S. DEPARTMENT OF ENERGY

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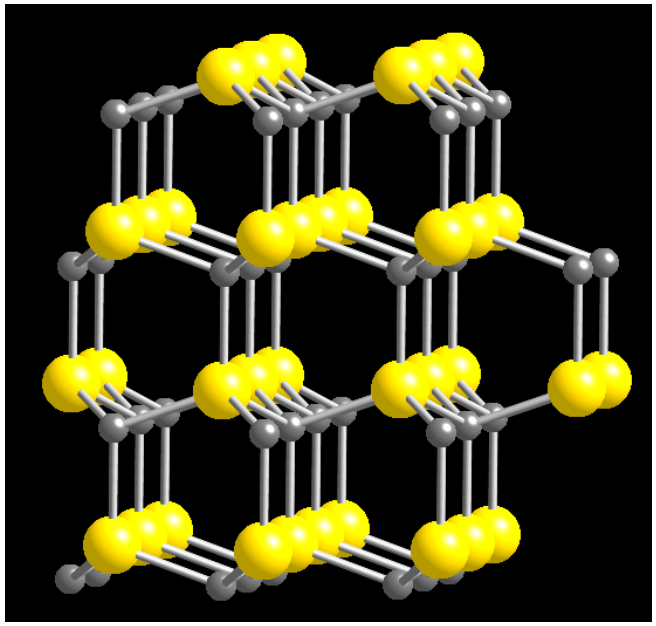
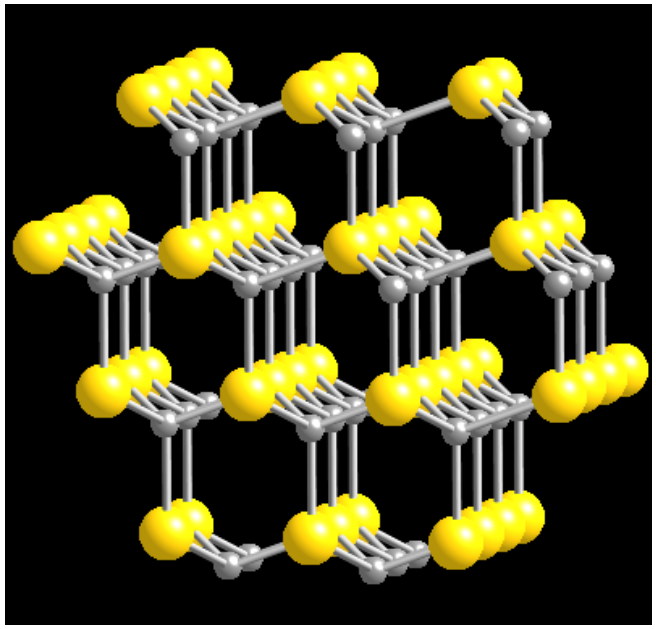
Preferential Synthesis

Is it possible to predictably synthesize one phase and not the other?



wurtzite

hcp



zinc blende

ccp

Los Alamos NATIONAL LABORATORY EST. 1943

Sharma, R. C.; Chang, Y. A. *J. Phys. Equil.* **1996** *17* 261.

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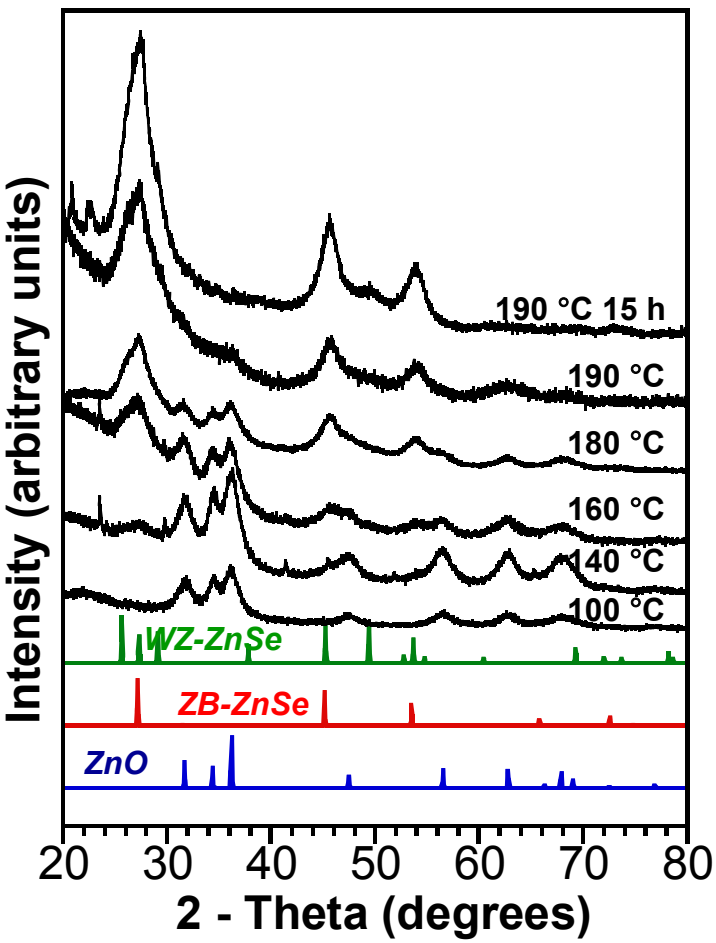
PENNSTATE 1855

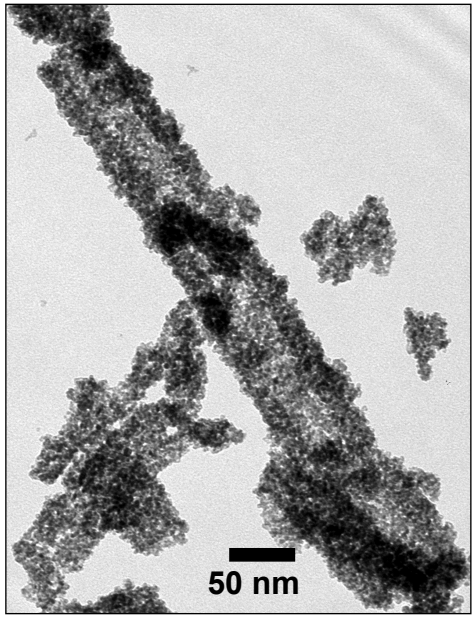
Control I: Extending to Synthesis of ZnSe

$ZnCl_2$ +TMAH $\xrightarrow[100\ °C]{EG}$ ZnO nanoparticles

ZnO nanoparticles $\xrightarrow{190\ °C}$ wurtzite – ZnSe nanoparticles

selenourea (in EG)





particles arrange into one dimensional arrays

Dawood, F.; Schaak, R. E. *J. Am. Chem. Soc.* **2009**, *131*, 424-425.

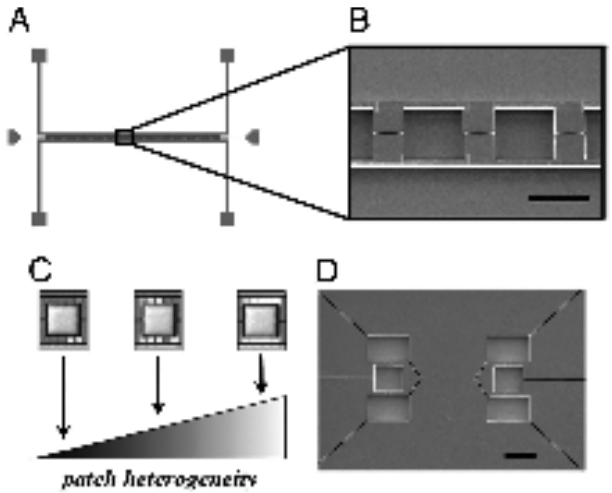
Outline

Part I: Colloidal Synthesis of Inorganic Nanocrystals

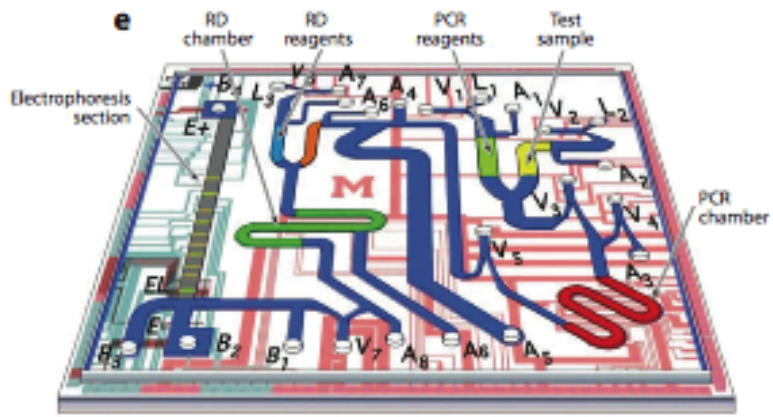
Part II: Nonlinear Optical Techniques

- Microfabrication in Aqueous Media
- Multiphoton Absorption Induced Luminescence of Metal Nanostructures

Microtechnologies for Aqueous Conditions



microhabitat patches for mimicking biological landscapes



chemical analysis and sensors

<u>Water</u>

inexpensive

non-toxic

biocompatible

Keymer, J. E.; Galajda, P.; Muldoon, C.; Park S.; Austin, R. H. *Proc. Nat. Acad. Sci. USA*, 2006, *103*, 17290-17295.

Livak-Dahl, E.; Sinn, I.; Burns, M. *Annu. Rev. Chem. Biomol. Eng.*, 2011, *2*, 325-353.

Challenge

To assemble a toolkit of microtechnologies for manipulating and fabricating/securing objects in aqueous media

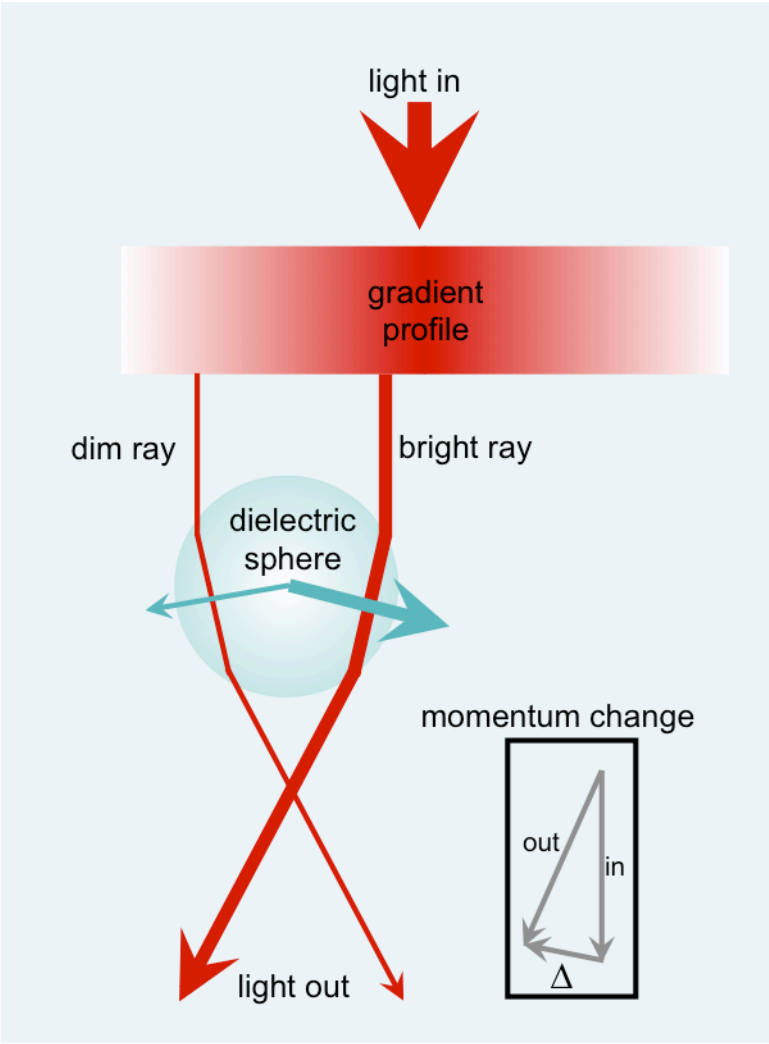
Challenge

To assemble a toolkit of microtechnologies for manipulating and fabricating/securing objects in aqueous media

Optical Techniques

1. ***Optical Tweezers*** *- maneuvering*
2. ***Multiphoton Absorption Polymerization*** *– fabricating*

Optical Tweezers



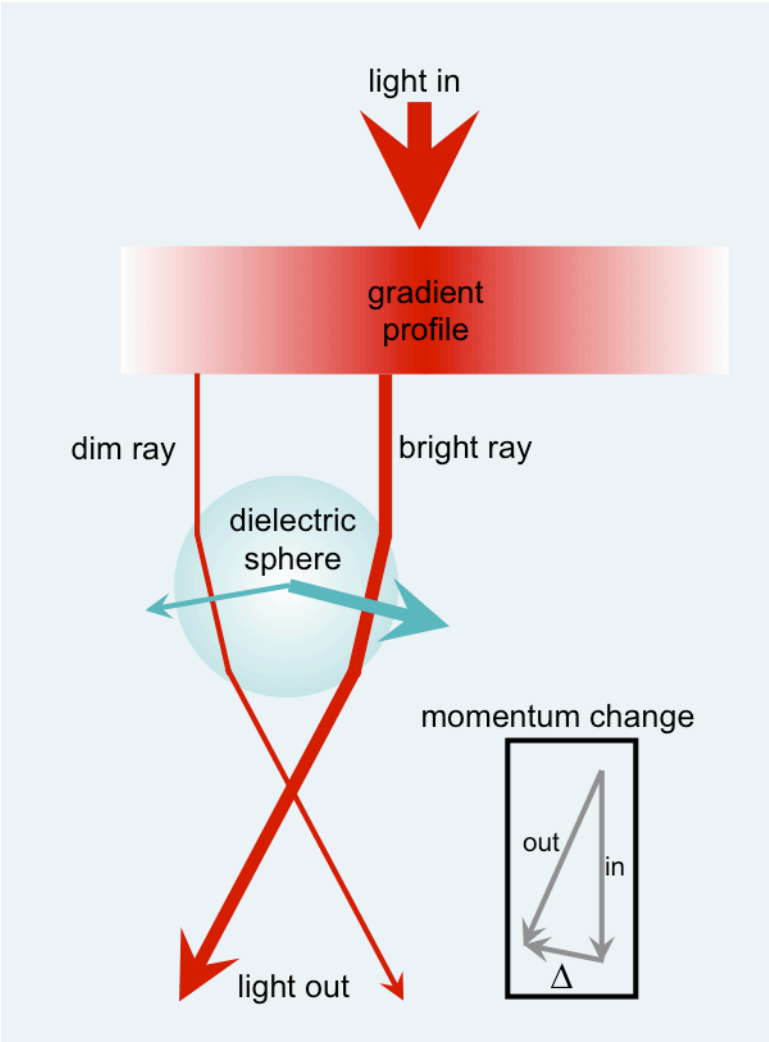
Required

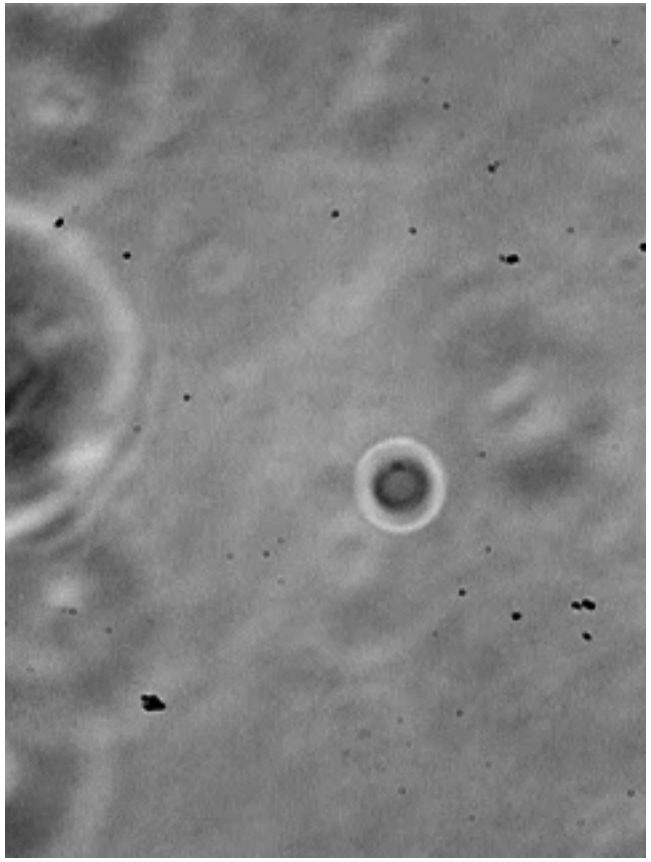
mismatch of refractive indices between object and medium

1. *change in momentum of light*
2. *equal and opposite force felt by sphere*
3. *sphere is pushed into the brightest part of the beam*

Dienerowitz, M.; Mazilu, M.; Dholakia, K. *J. Nanophotonics* 2008, *2*, 1-32.
Svoboda, K.; Block, S. M. *Annu. Rev. Biophys. Biomol. Struct.* 1994, *23*, 247.

Optical Tweezers





Dienerowitz, M.; Mazilu, M.; Dholakia, K. *J. Nanophotonics* 2008, *2*, 1-32.
Svoboda, K.; Block, S. M. *Annu. Rev. Biophys. Biomol. Struct.* 1994, *23*, 247.

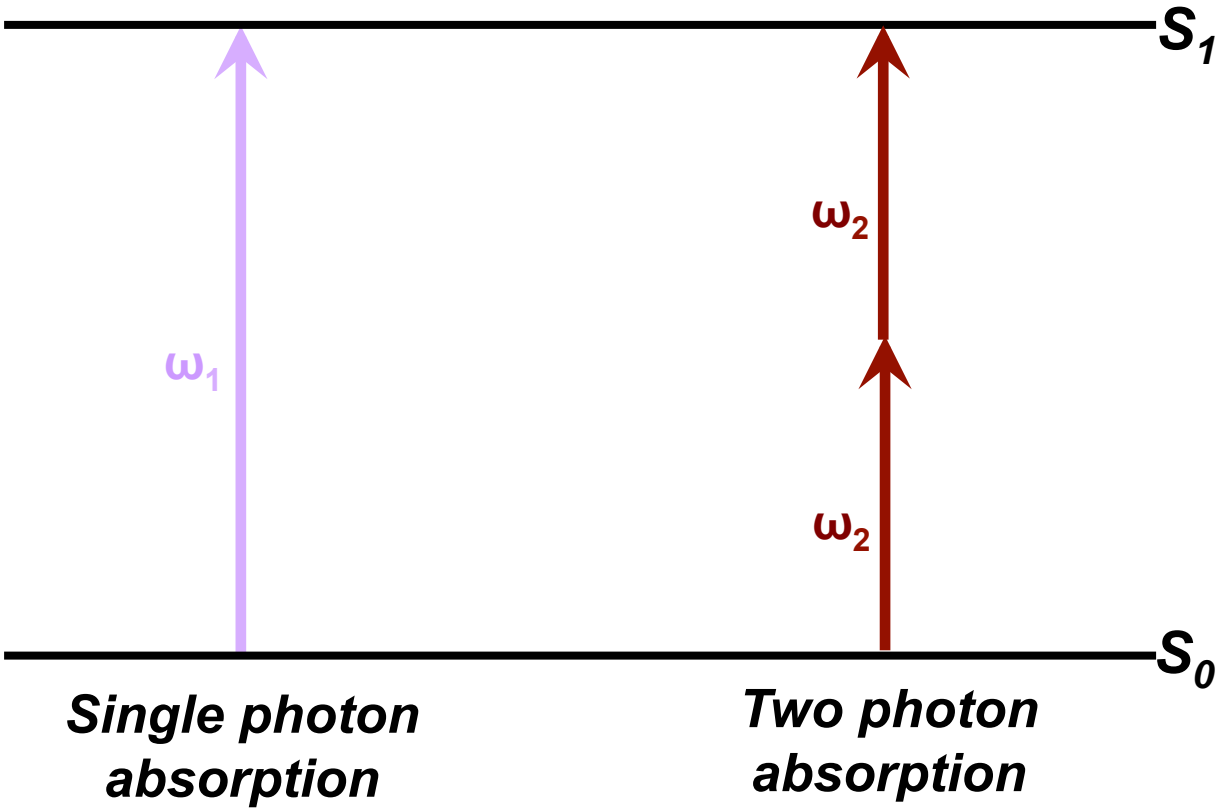
Challenge

To assemble a toolkit of microtechnologies for manipulating and fabricating/securing objects in aqueous media

Optical Techniques

1. ***Optical Tweezers*** *- maneuvering*
2. ***Multiphoton Absorption Polymerization*** *– fabricating*

Multiphoton Absorption (MPA)

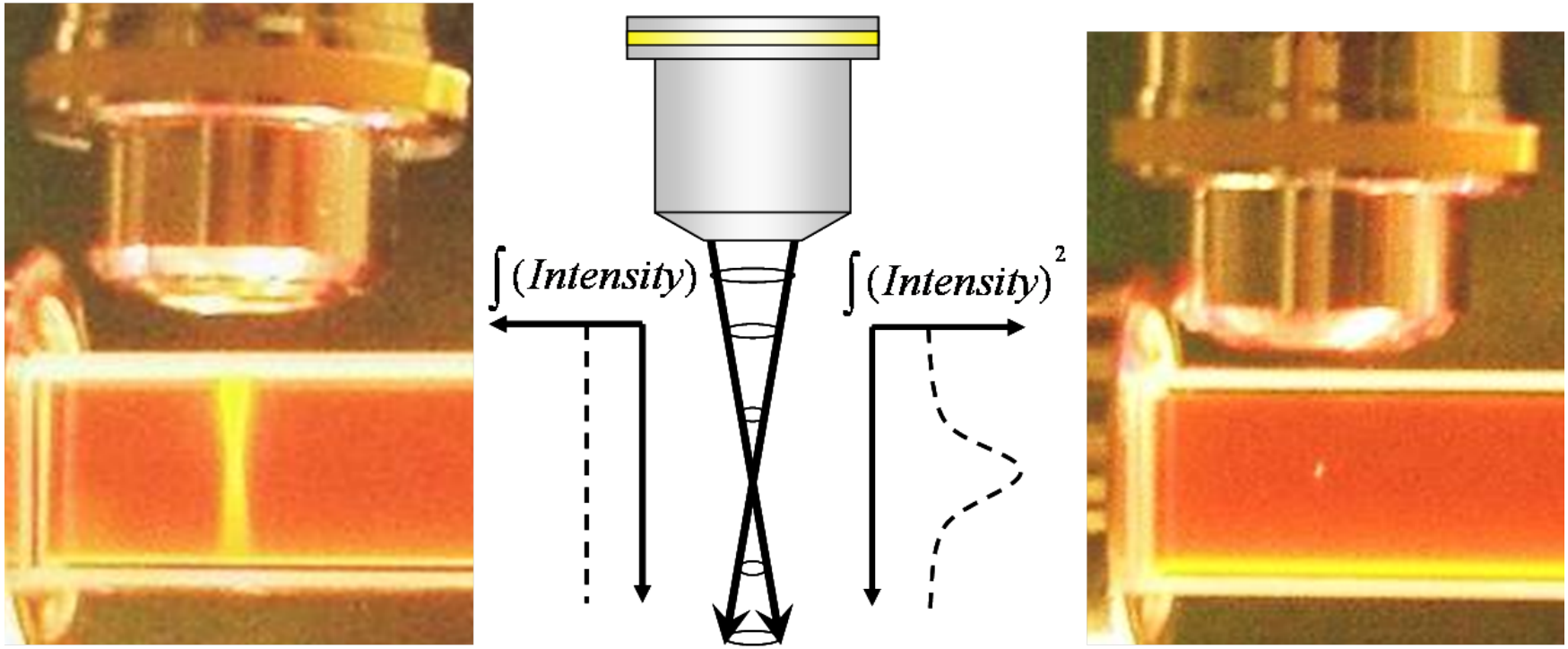


probability of MPA ~ I^n

I = Intensity

n = number of photons

Multiphoton Absorption(MPA)



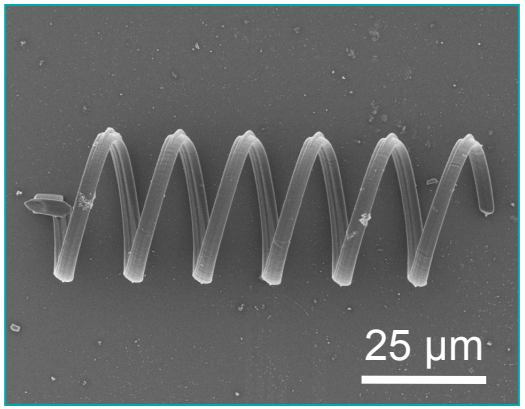
single photon absorption

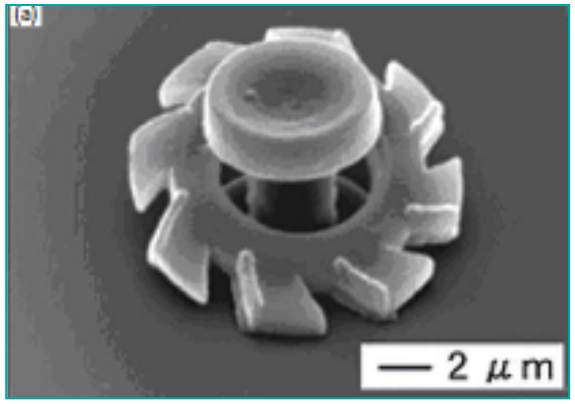
two photon absorption

MPA allows for site-specific photochemistry

LaFratta, C. N.; Fourkas, J. T.; Baldacchini T.; Farrer, R. A. *Angew. Chem. Int. Ed.*, 2007, *46*, 6238-6258.

Multiphoton Absorption Polymerization (MAP)





Photoresist

Monomers

Photoinitiator

mostly carried out in neat photoresists/ organic solvents

MAP of proteins - typically use photosensitizers

can remain in protein matrix and regenerate singlet oxygen

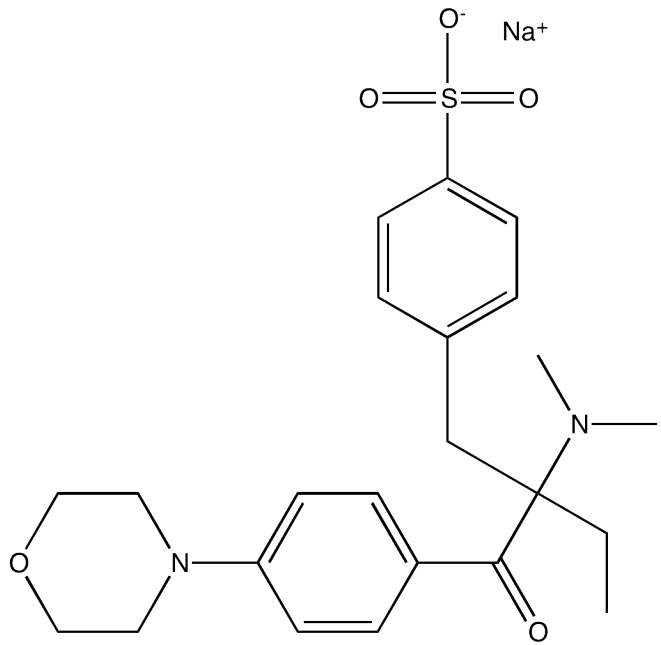
can be detrimental to cell viability

Maruo, S., et al., J. Microelectromech. Syst. (2003) 12, 533

LaFratta, C. N.; Fourkas, J. T.; Baldacchini T.; Farrer, R. A. *Angew. Chem. Int. Ed.*, 2007, *46*, 6238-6258.

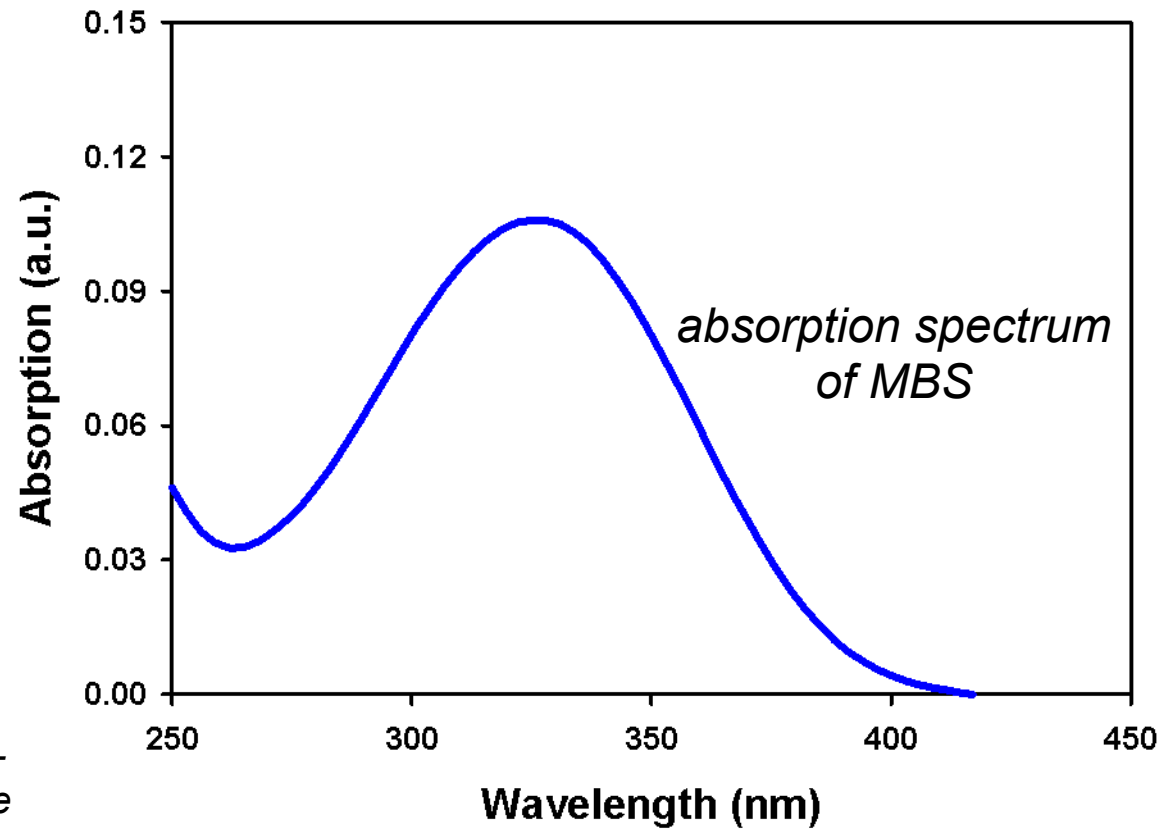
Kaehr, B.; Shear, J. B. *J.Am. Chem.Soc.* **2007**, *129*, 1904.

Water-soluble Photoinitiator (MBS)



MBS

sodium 4-[2-(4-morpholino)benzoyl-2-dimethylamino] butylbenzenesulfonate



decomposes into smaller fragments

can be easily washed away

minimal residual photoactivity when exposed to visible light

Kojima, K.; Ito, M.; Morishita, H.; Hayashi, N. *Chem. Mater.*, 1998, *10*, 3429-3433.

Dawood, F.; Qin, S.; Li, L.; Lin, E. Y.; Fourkas, J. T. *Chem. Sci.* 2012, *3*, 2449.

Materials used in Photoresists

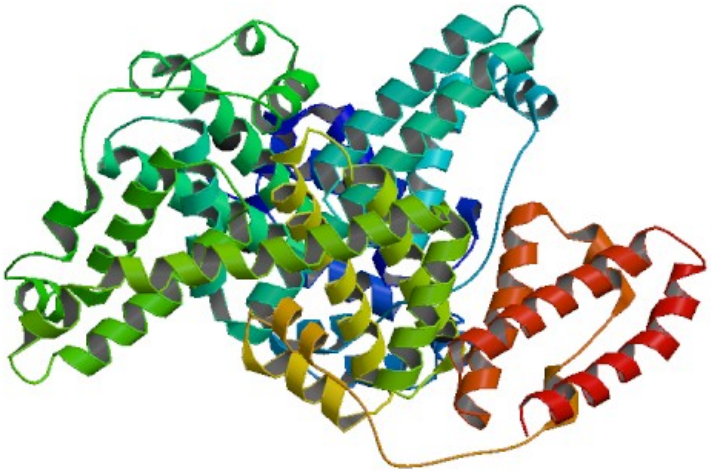
low refractive index

low viscosity

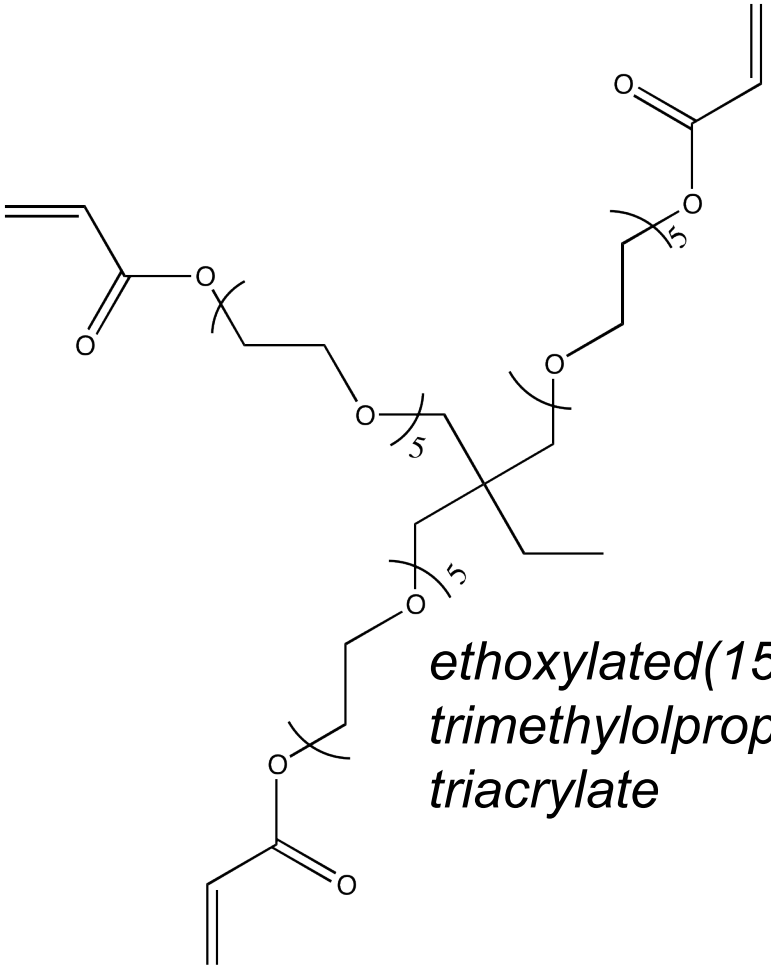
robust structures

tunable mechanical properties

large processing window



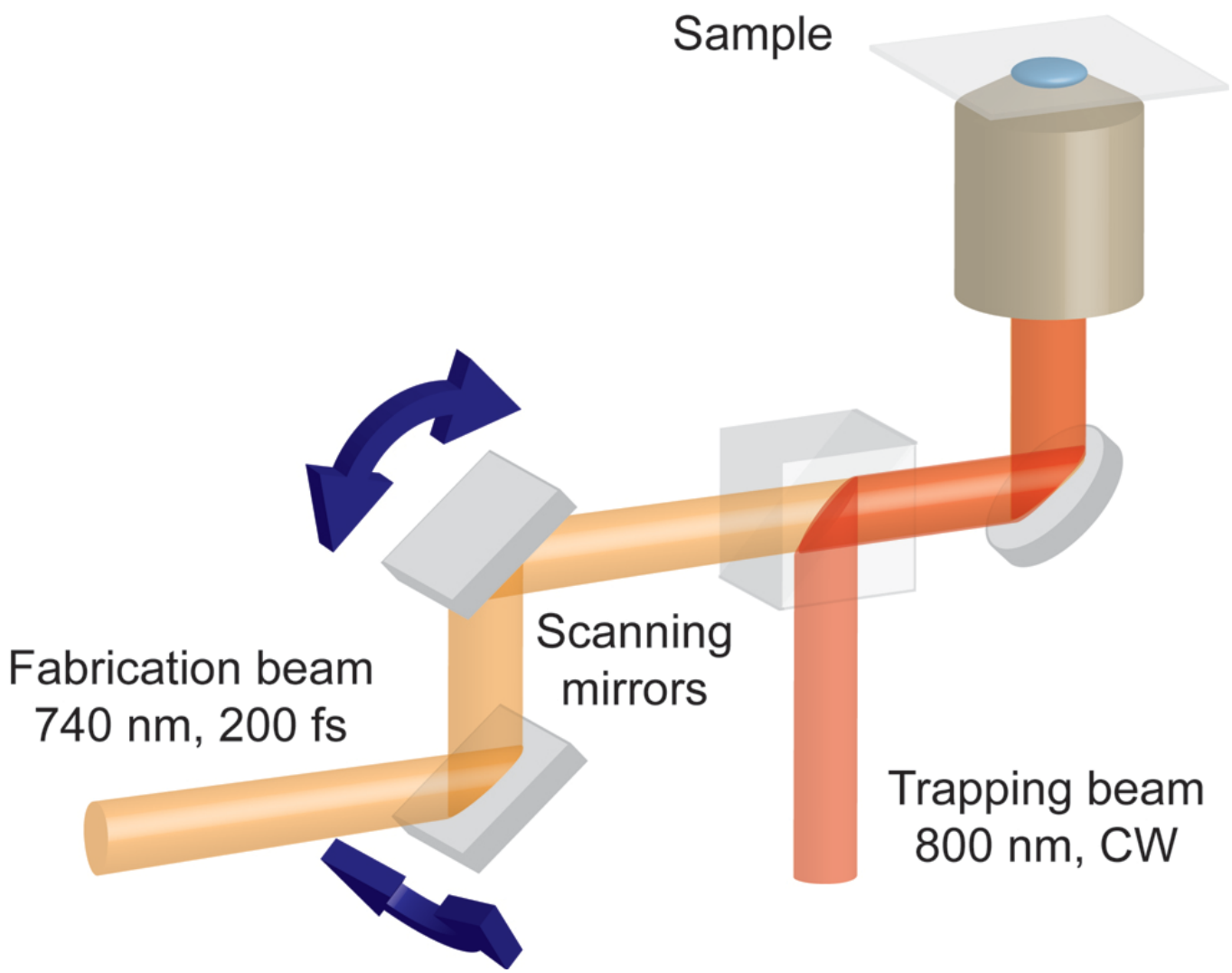
bovine serum albumin (BSA)



ethoxylated(15) trimethylolpropane triacrylate

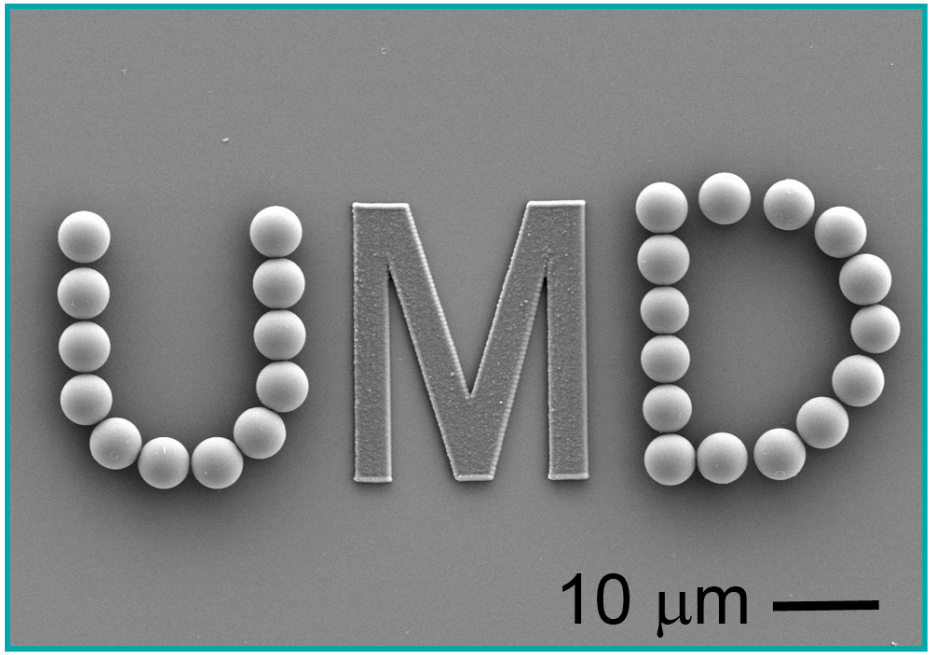
-COOH silica microbeads were incorporated for optical trapping

Combining Optical Tweezers and MAP



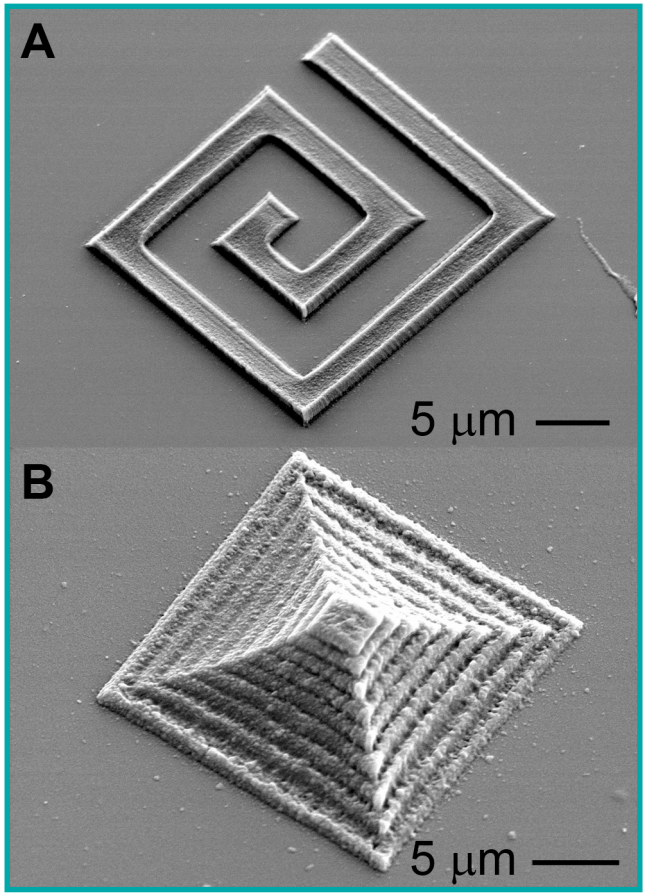
Dawood, F.; Qin, S.; Li, L.; Lin, E. Y.; Fourkas, J. T. *Chem. Sci.* 2012, *3*, 2449.

Microstructures in Water- Based Media



"U" and "D" – assembled with microbeads

"M" – fabricated with acrylate



microstructures fabricated with BSA

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Dawood, F.; Qin, S.; Li, L.; Lin, E. Y.; Fourkas, J. T. *Chem. Sci.* 2012, *3*, 2449.

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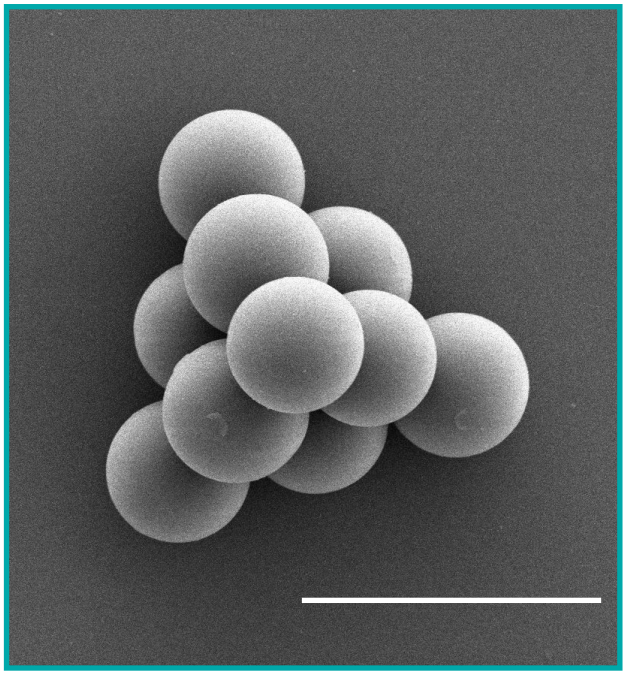
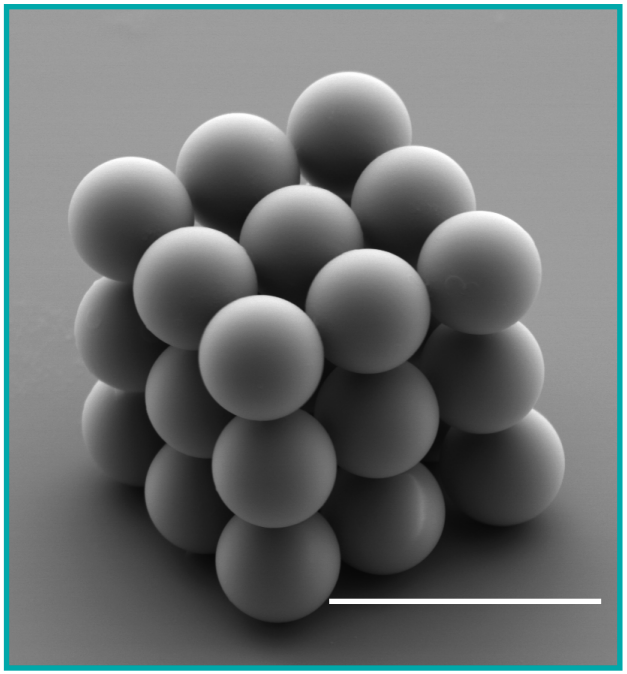
3D Structures (Silica Microspheres)



Pyramid
optimal contact



3 x 3 Cube
minimal contact

each microsphere was positioned using optical tweezers and secured with MAP of the water-soluble photoresist (scale bar 10 µm)

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Dawood, F.; Qin, S.; Li, L.; Lin, E. Y.; Fourkas, J. T. *Chem. Sci.* 2012, *3*, 2449.

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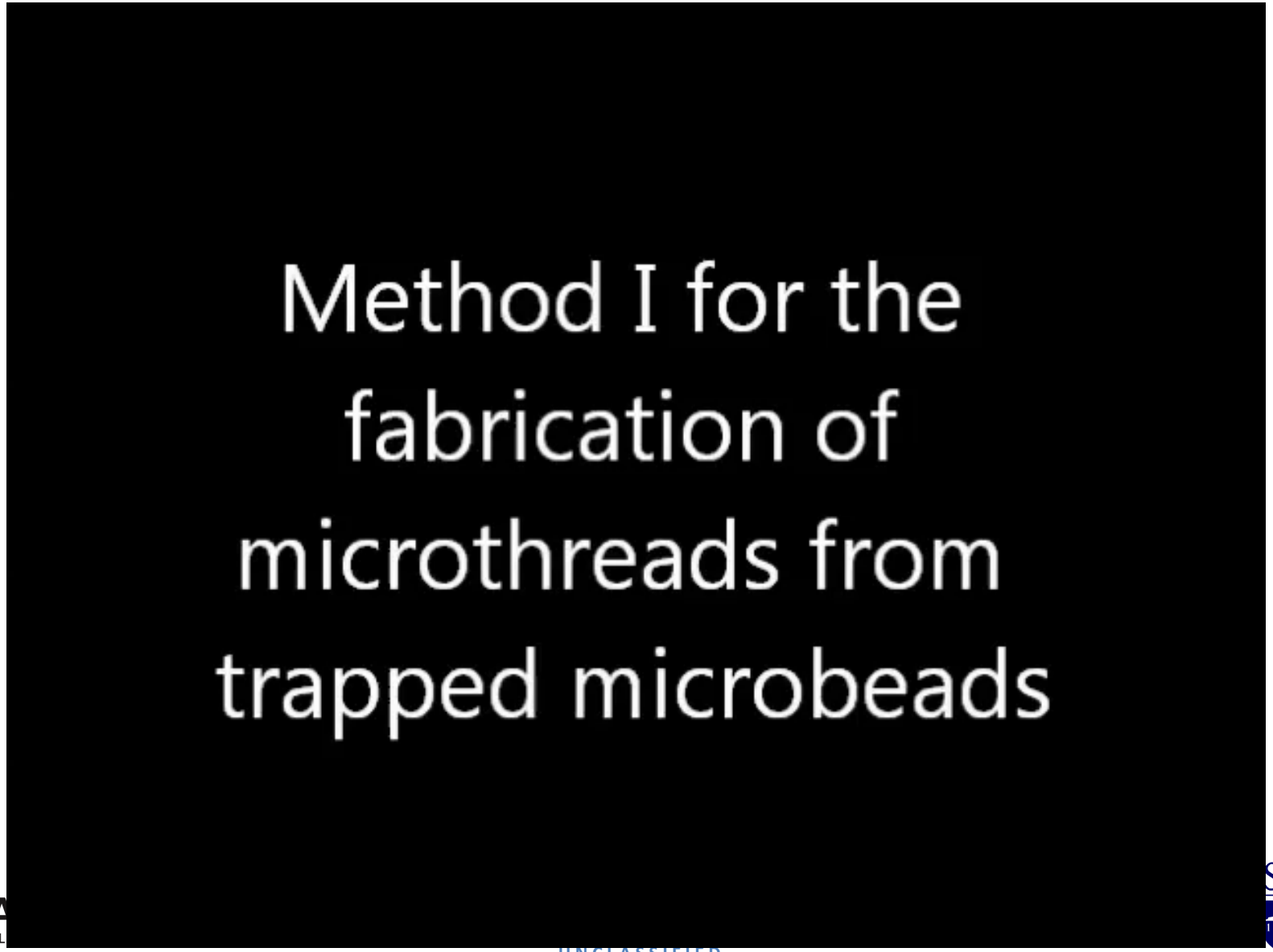
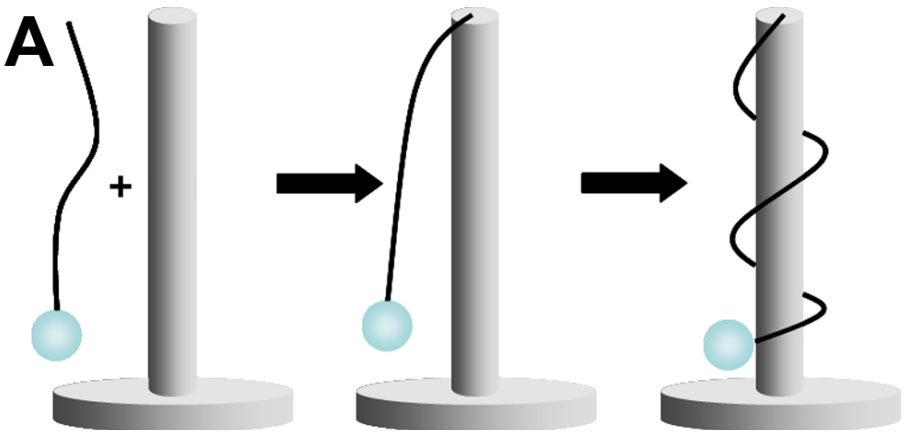
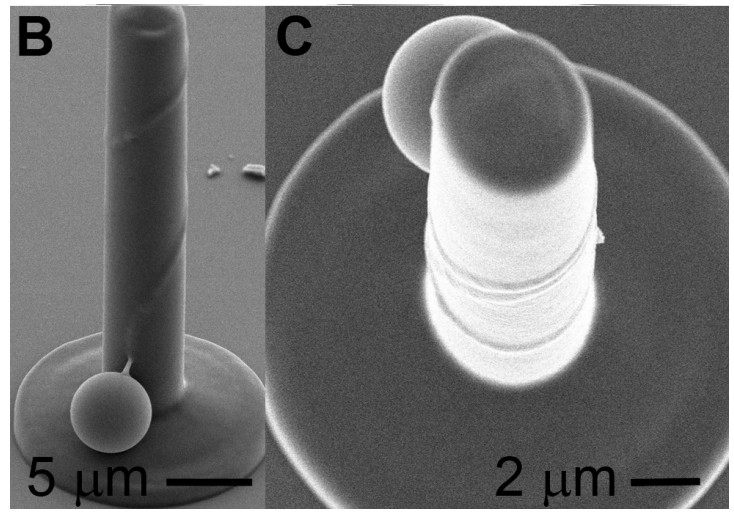
Fabrication of Microthreads – Method I

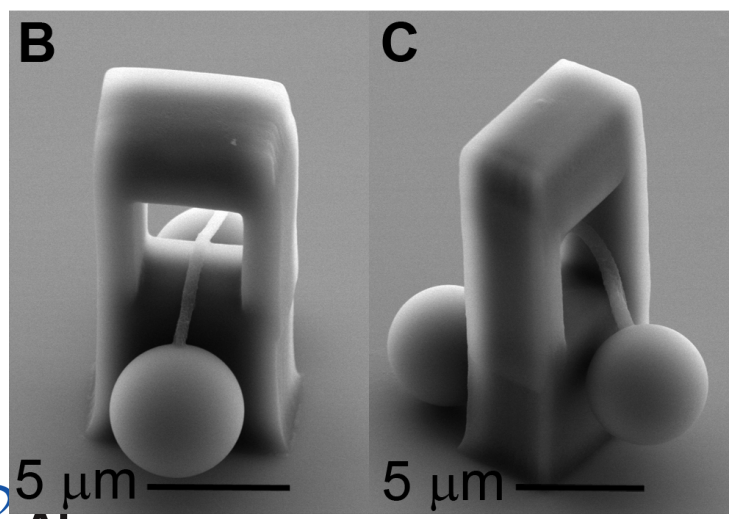


Fabrication of Microthreads

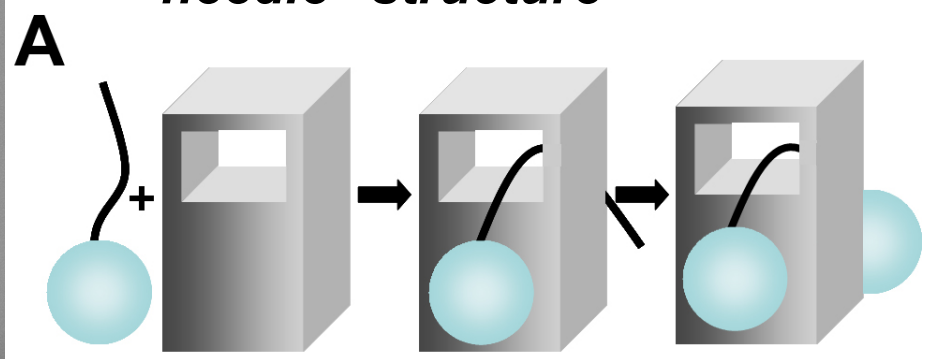
"tetherball" structure







"needle" structure



Dawood, F.; Qin, S.; Li, L.; Lin, E. Y.; Fourkas, J. T. *Chem. Sci.* 2012, *3*, 2449.

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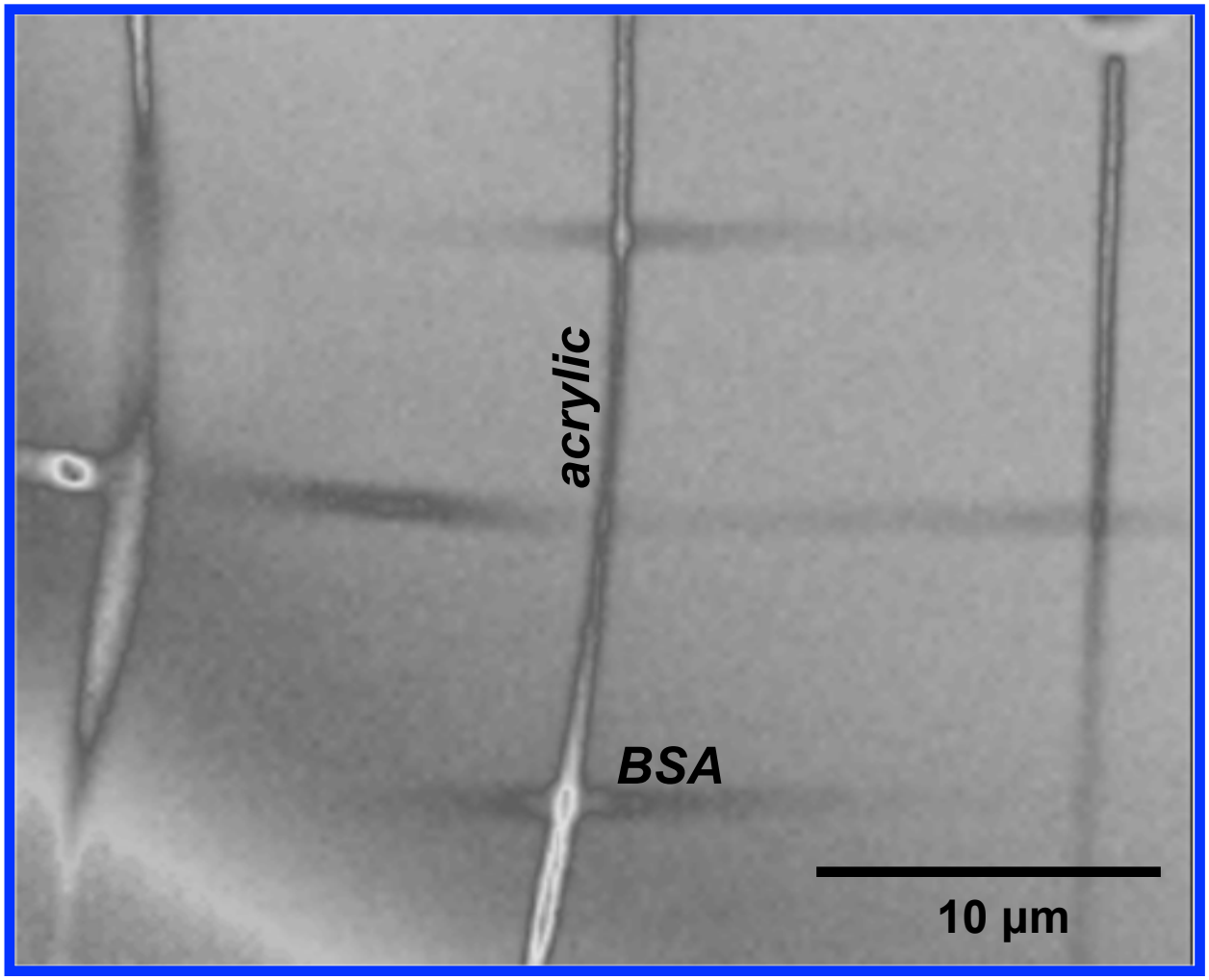
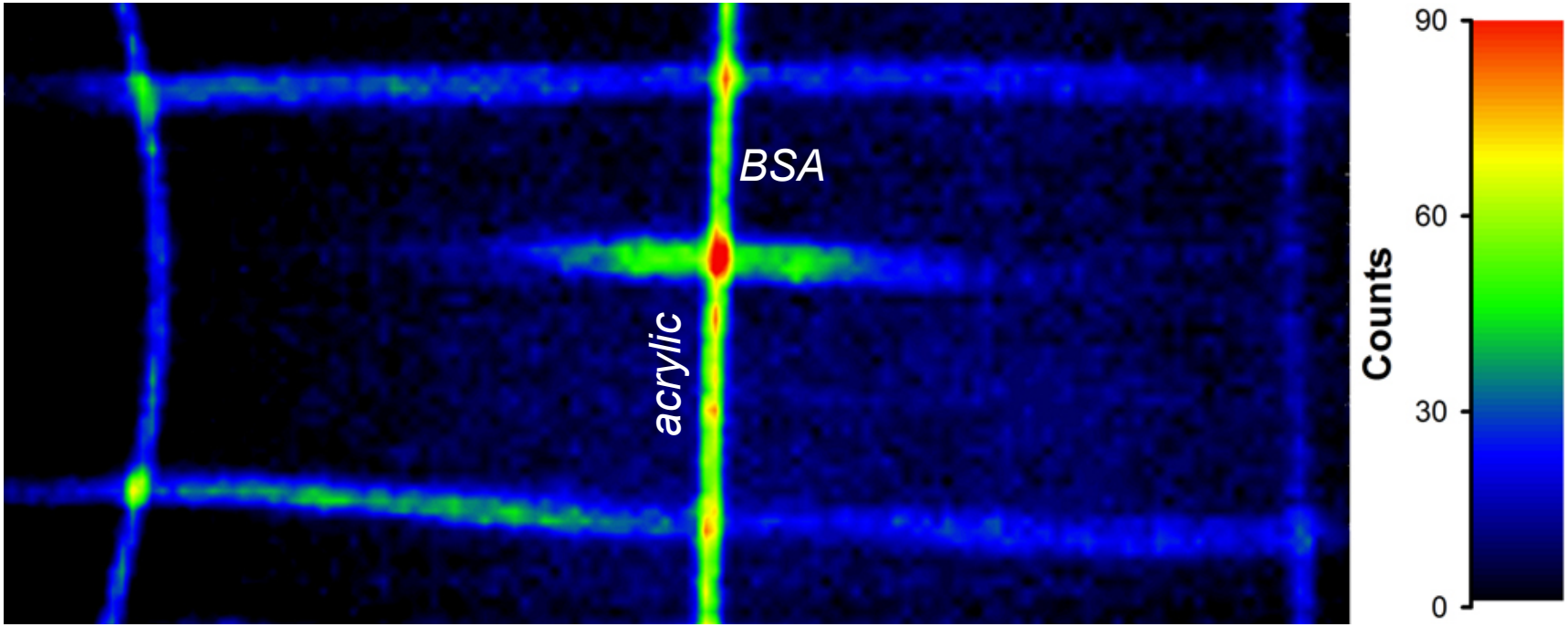
BSA Microthreads for Microweaving



microwoven threads

Dawood, F.; Qin, S.; Li, L.; Lin, E. Y.; Fourkas, J. T. *Chem. Sci.* 2012, Advanced Article.

BSA Microthreads for Microweaving



two-photon fluorescence image of microwoven threads

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Dawood, F.; Qin, S.; Li, L.; Lin, E. Y.; Fourkas, J. T. *Chem. Sci.* 2012, Advanced Article.

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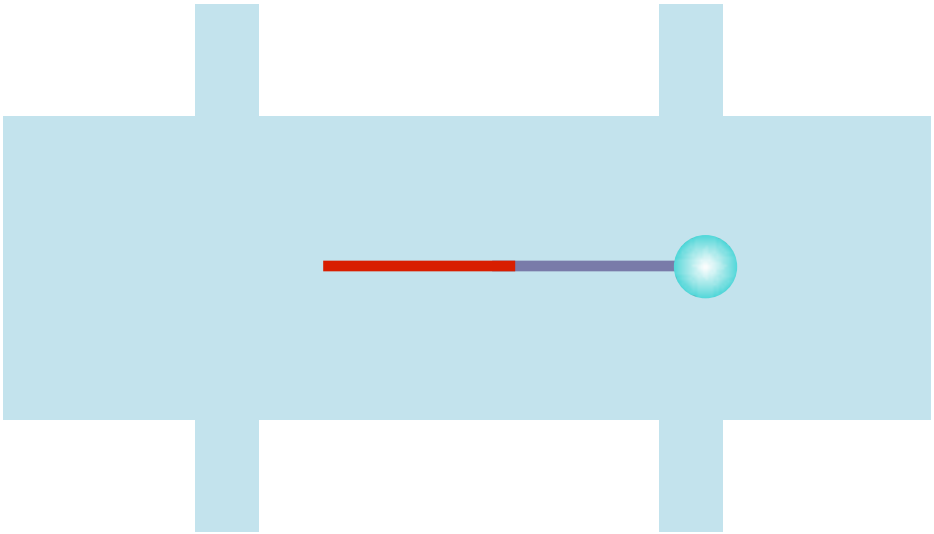
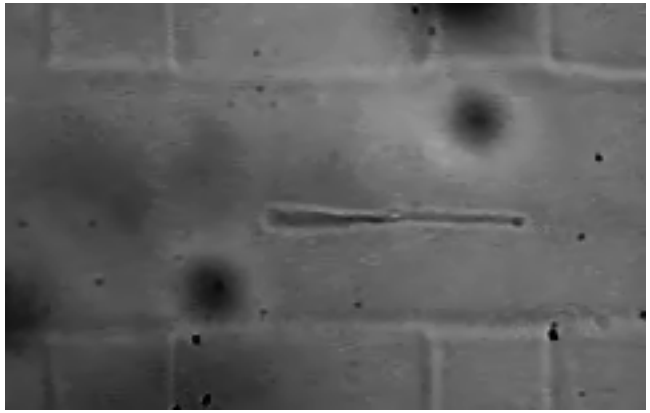
Fabricating Multicomponent Microthreads

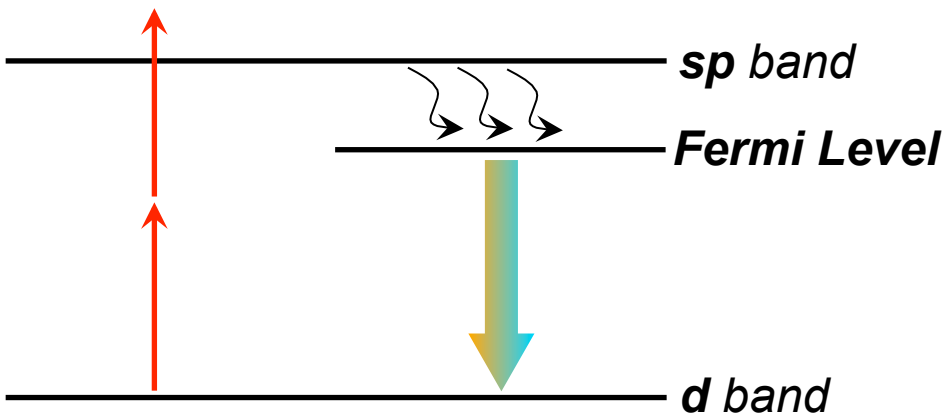


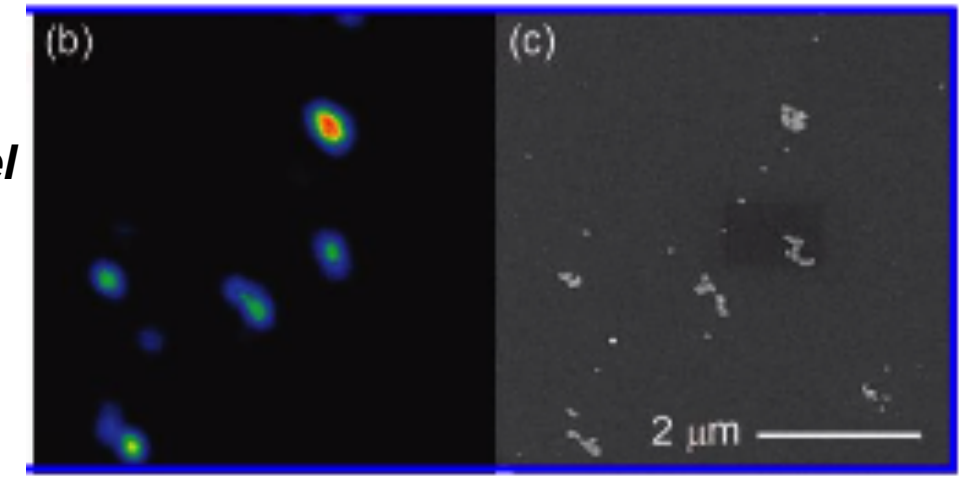
Low viscosity of photoresist allows it to be introduced into microfluidic devices



Allows for the fabrication of microcomponent microthreads

Multiphoton Absorption Induced Luminescence (MAIL)





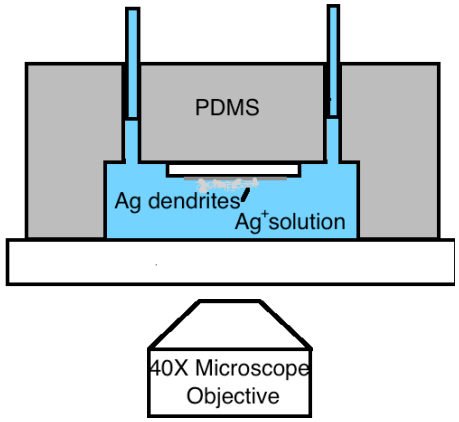
Field enhancement increases the probability of multiphoton absorption

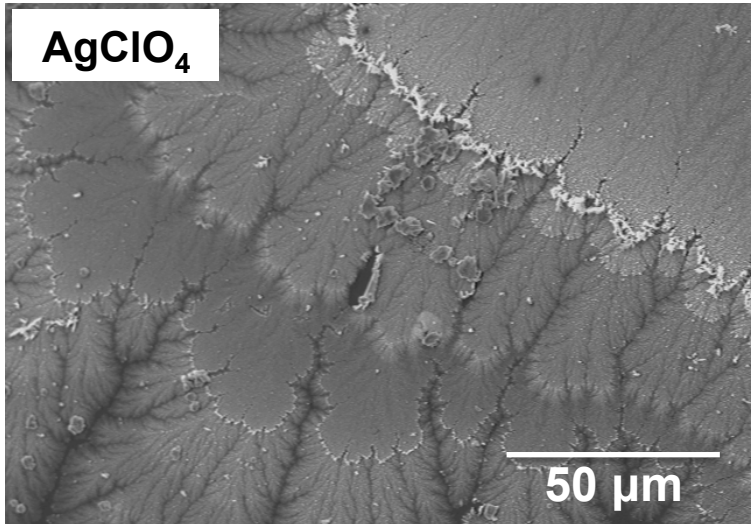
Absorption of multiple photons can lead to efficient luminescence of a noble metal nanostructure

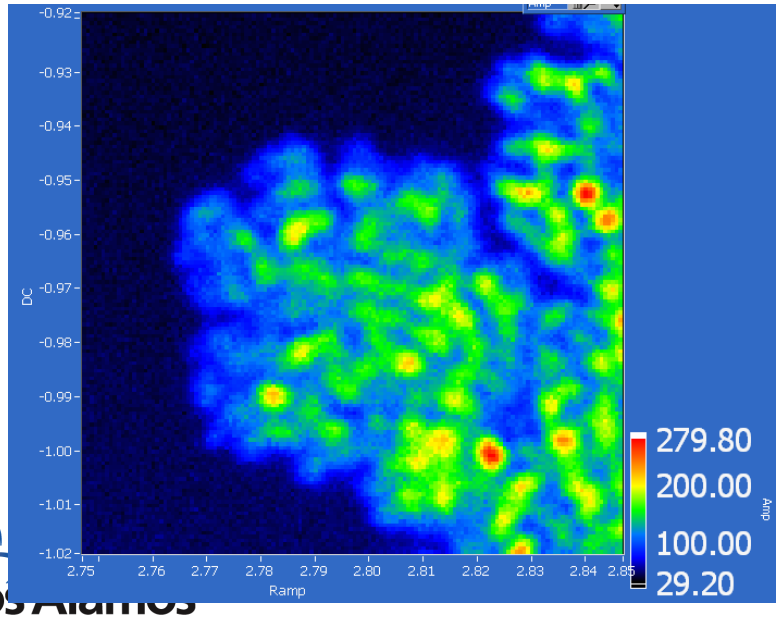
Fourkas, J.T. *et. al. J. Phys. Chem. B,* **2009**, *113*, 4416 – 4422.

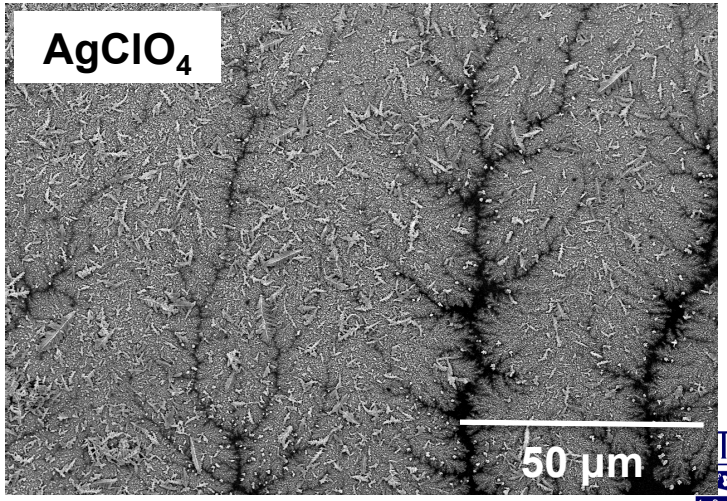
Galvanic Displacement Reactions for Silver Dendritic "Plates"

$$Al_{(s)} + 3Ag^{+}_{(aq)} \rightarrow 3Ag_{(s)} + Al^{3+}_{(aq)} \quad E° = +2.46\ V$$



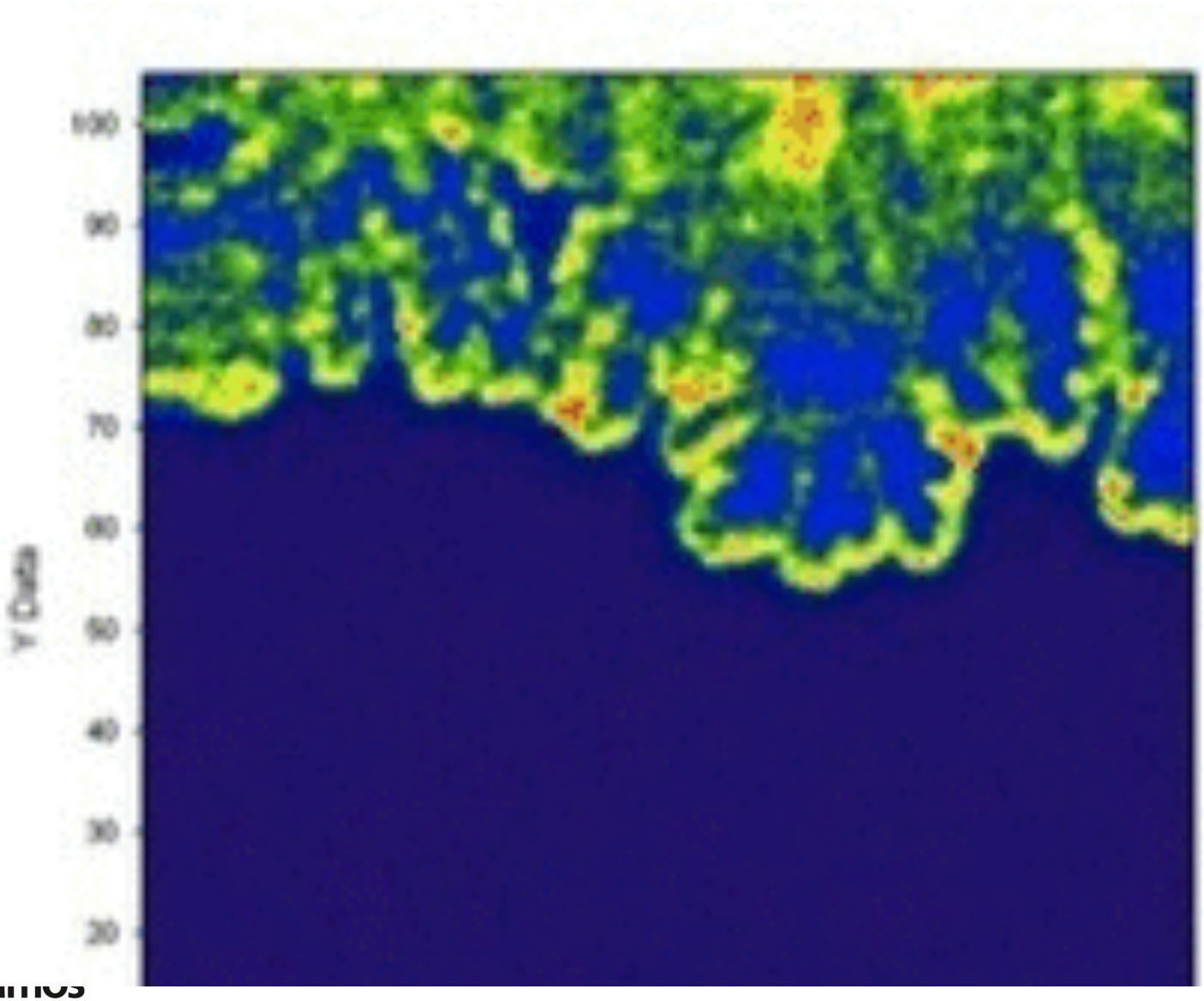






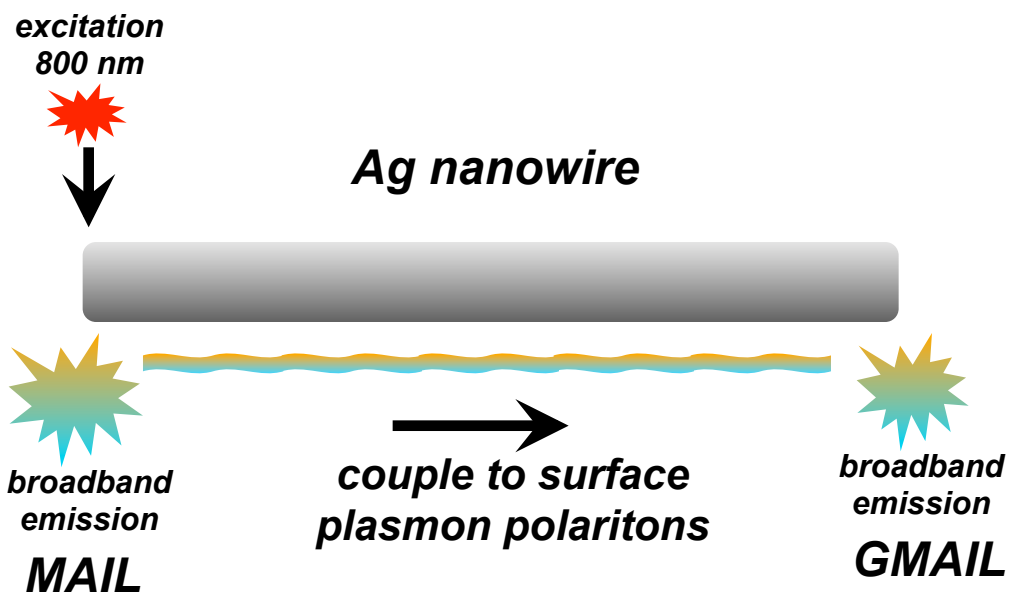
Dawood, F. Hsu, M. in preparation.

In-situ Monitoring of Growth Process with MAIL



Dawood, F. Hsu, M. in preparation.

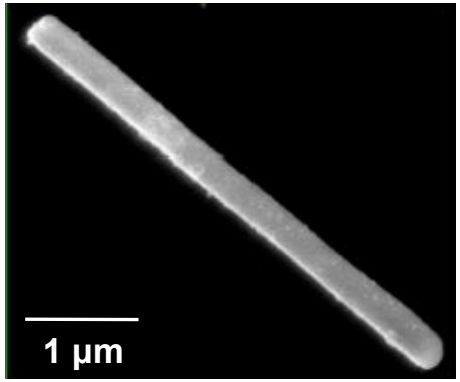
Multiphoton Absorption and Broadband Waveguiding in Metal Nanowires

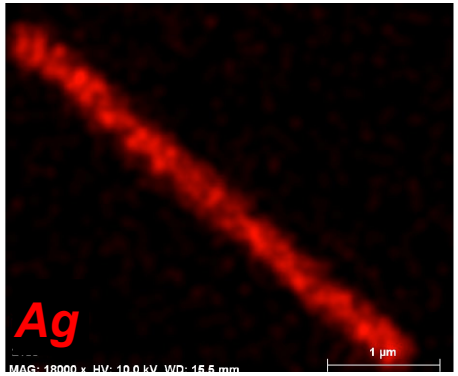


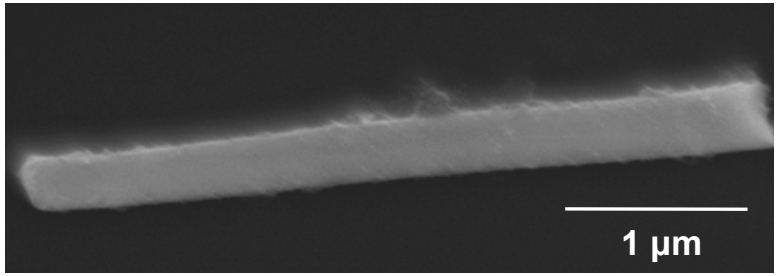
Multiphoton Absorption Induced Luminescence

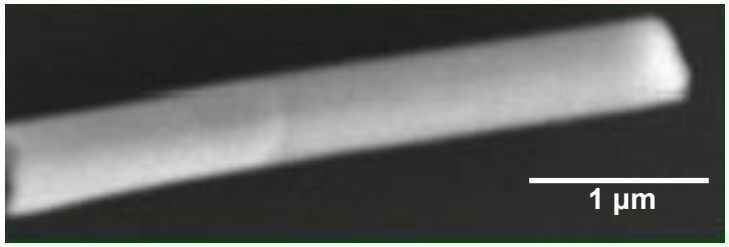
Guided Multiphoton Absorption Induced Luminescence

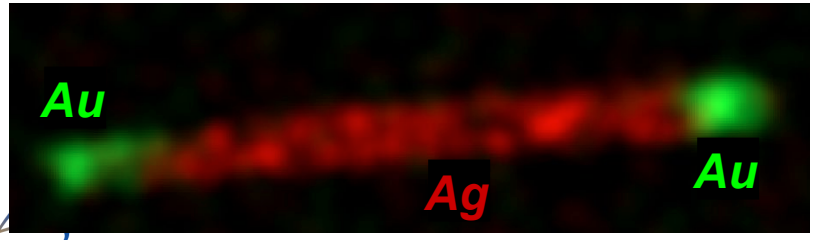
Multimetal Nanowires using AAO Membranes

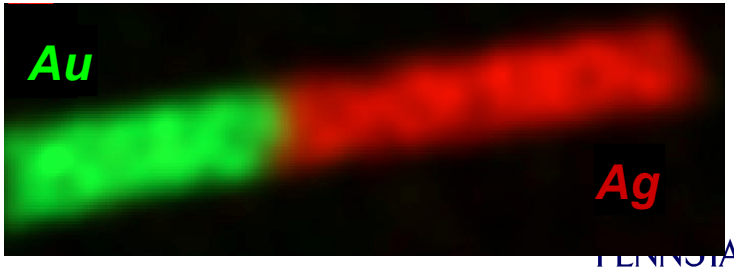




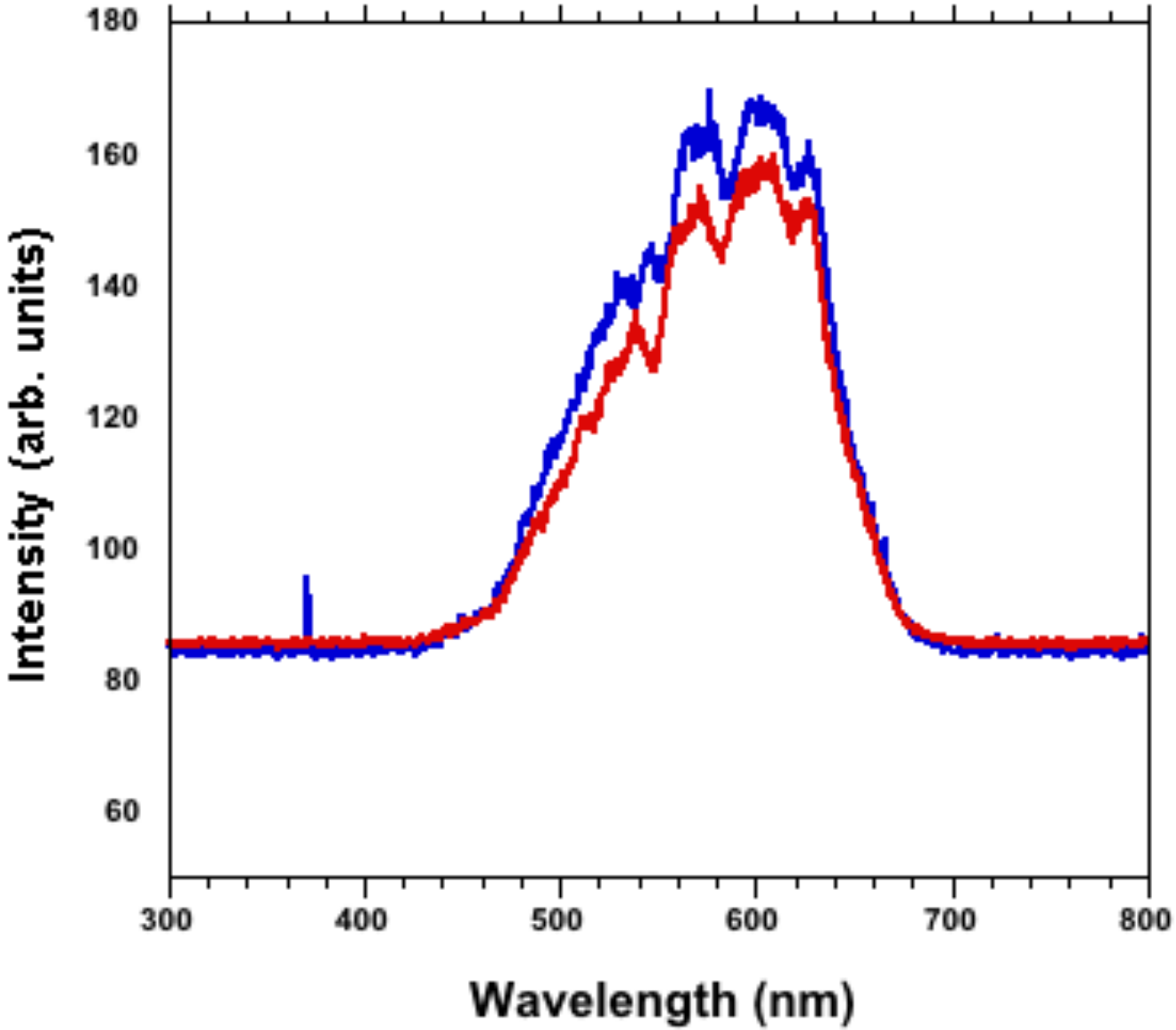








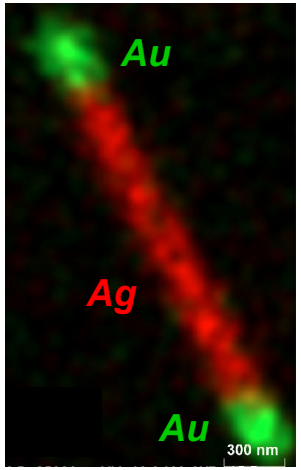
Emission Spectra of Silver Nanowires

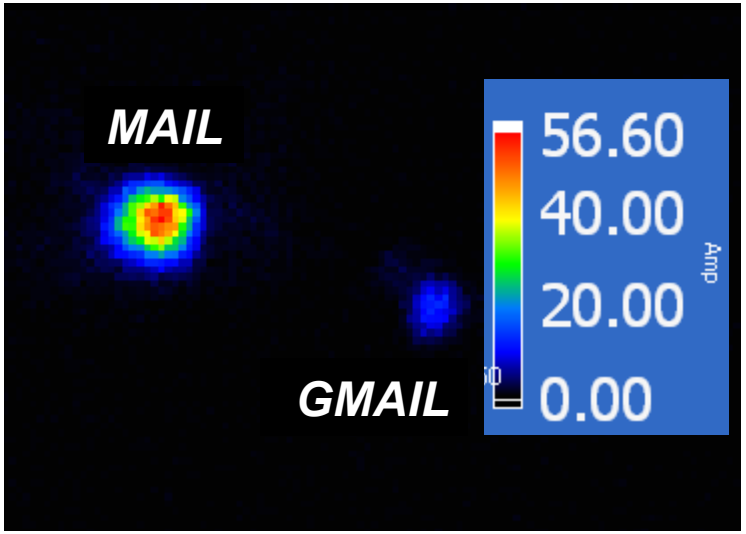


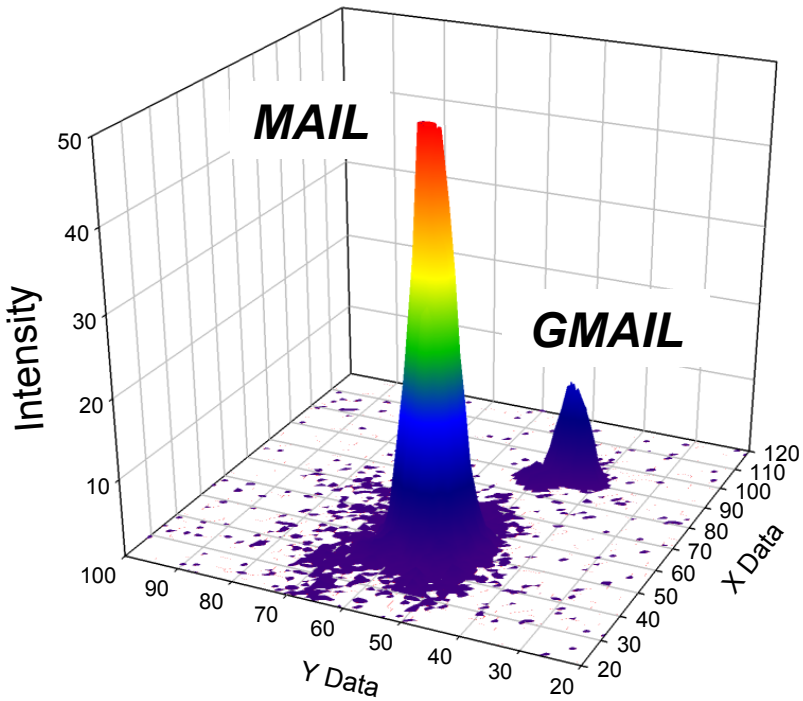
proximal end (MAIL)

distal end (GMAIL)

MAIL of Au-Ag-Au Nanowires



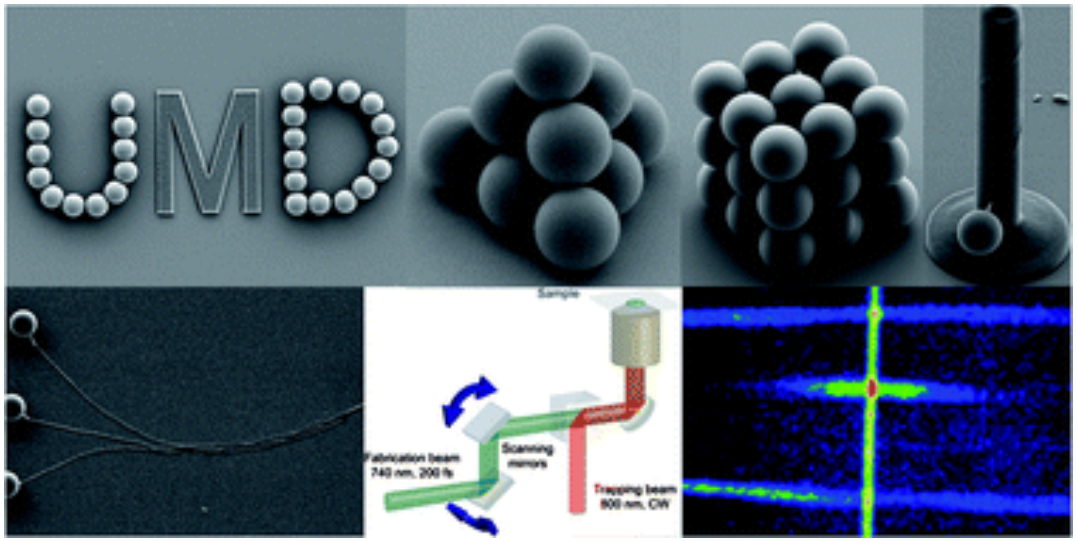




3.5 µm Au-Ag-Au nanowire excited at 800 nm (~1 mW)

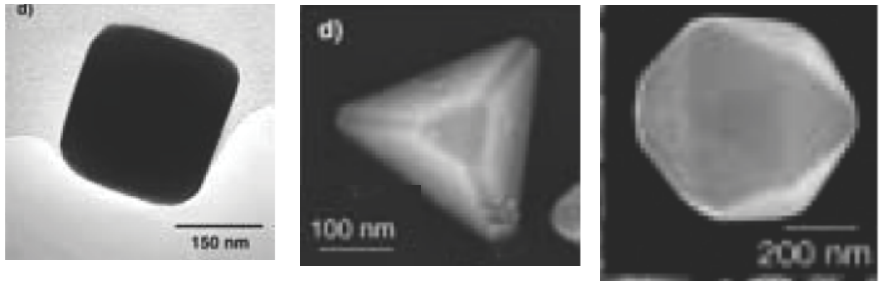
Conclusions – Nonlinear Methods

- Simultaneous fabrication (MAP) and manipulation (optical tweezers) has been demonstrated in aqueous media
- Multiphoton Absorption Induced Luminescence (MAIL) can easily couple into the plasmon mode of dendritic silver plates and metal nanowires



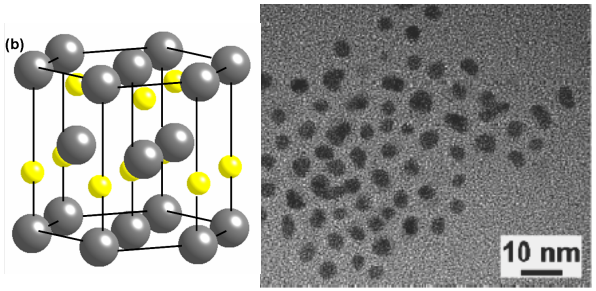
Advantages of Liquid-Phase Methods

morphology



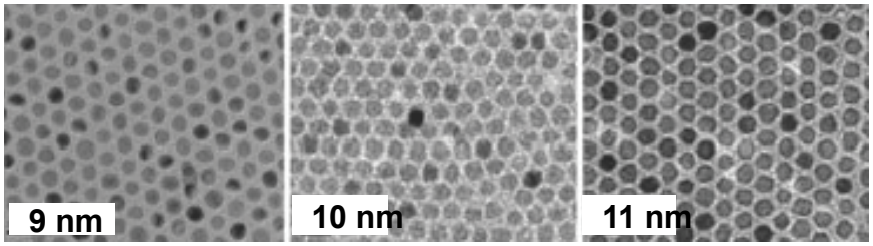
Au – 280 °C

metastable phases



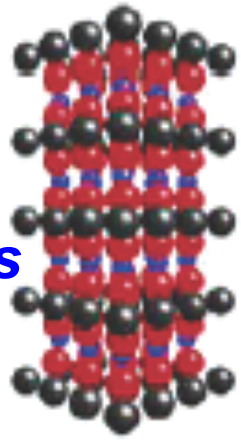
wurtzite - ZnS – 160 °C

size



Fe_3O_4 - 280 °C

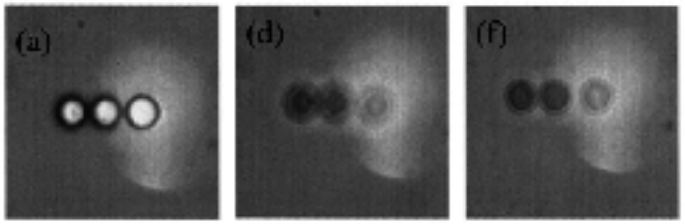
new materials



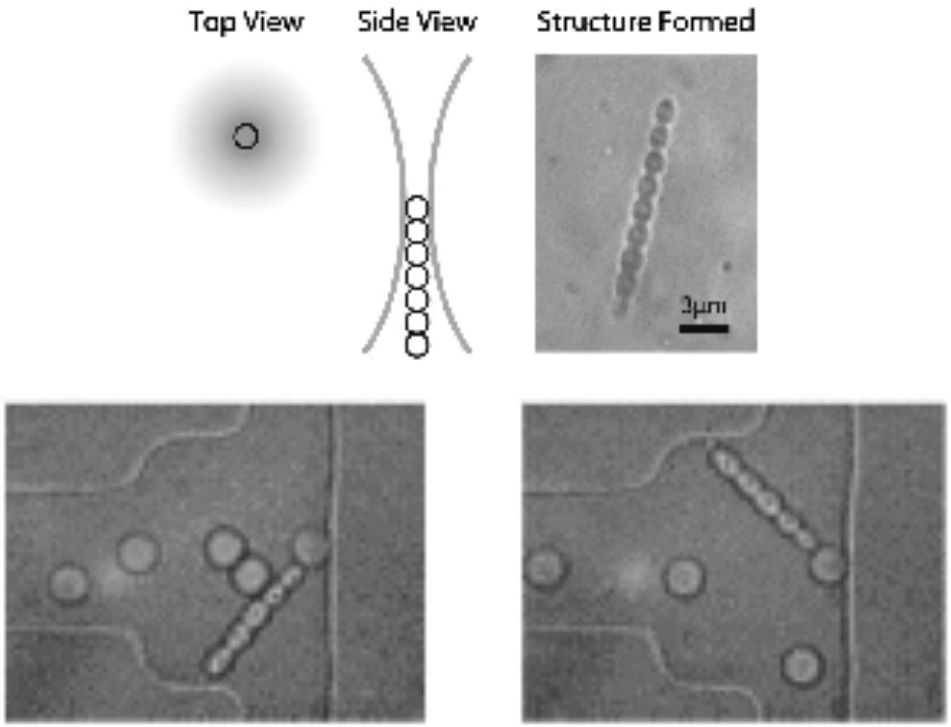
$AuCuSn_2$ – 200 °C

Zhao, Y.; Zhang, Y.; Zhu, H.; Hadjipanayis, G. C.; Xiao, J. Q. *J. Am. Chem. Soc.* **2004**, *126*, 6874-6875.
Kim, F.; Connor, S.; Song, H.; Kuykendall, T.; Yang, P. *Angew. Chem. Int. Ed.* **2004**, *43*, 3673-3677.
Leonard, B. M.; Bhuvanesh, N. S. P.; Schaak, R. E. *J. Am. Chem. Soc.* **2005**, *127*, 7326-7327.
Hyeon, T. et. al. *Angew. Chem. Int. Ed.* **2005**, *44*, 2872-2877.

Optical Tweezers for Immobilization



particles are fixed onto a surface

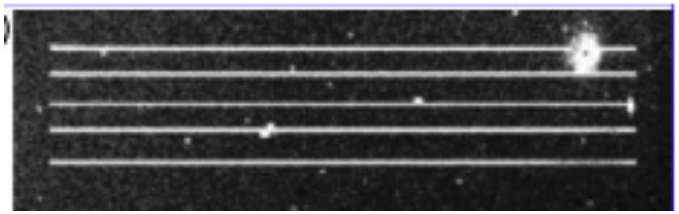


particles are attached to eachother, but only in linear arrangement

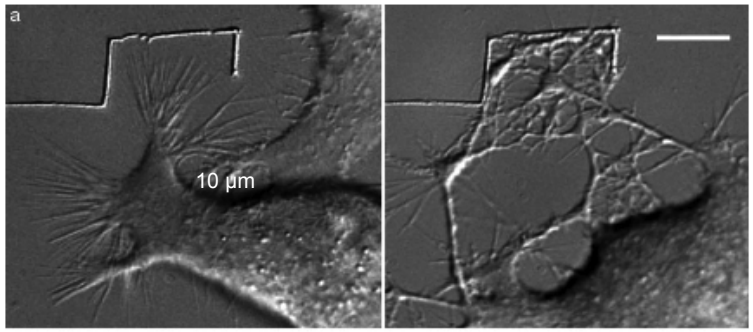
location of fabrication is limited

Masuhara et. al. *Appl. Phys. Lett.* 1992, *60*, 310.
Terray, A.. Oakey, J.; Marr, D. W. M. *Appl. Phys. Lett.* 2002, *81*, 1555.

MAP for Biomolecular Microstructures



MAP of collagen



walls made of BSA can confine neuronal growth

typically use photosensitizers – can be generated after some time
can remain in protein matrix and regenerate singlet oxygen
can be detrimental to cell viability
expensive alternative – flavine adenine dinucleotide (FAD)

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Campagnola, P. J. et. al. *Biomacromolecules* 2005, *6*, 1465.
Shear, J. B. et. al. *PNAS* 2004, *101*, 16105.
Kaehr, B.; Shear, J. B. *J. Am. Chem. Soc.* 2007, *129*, 1904.

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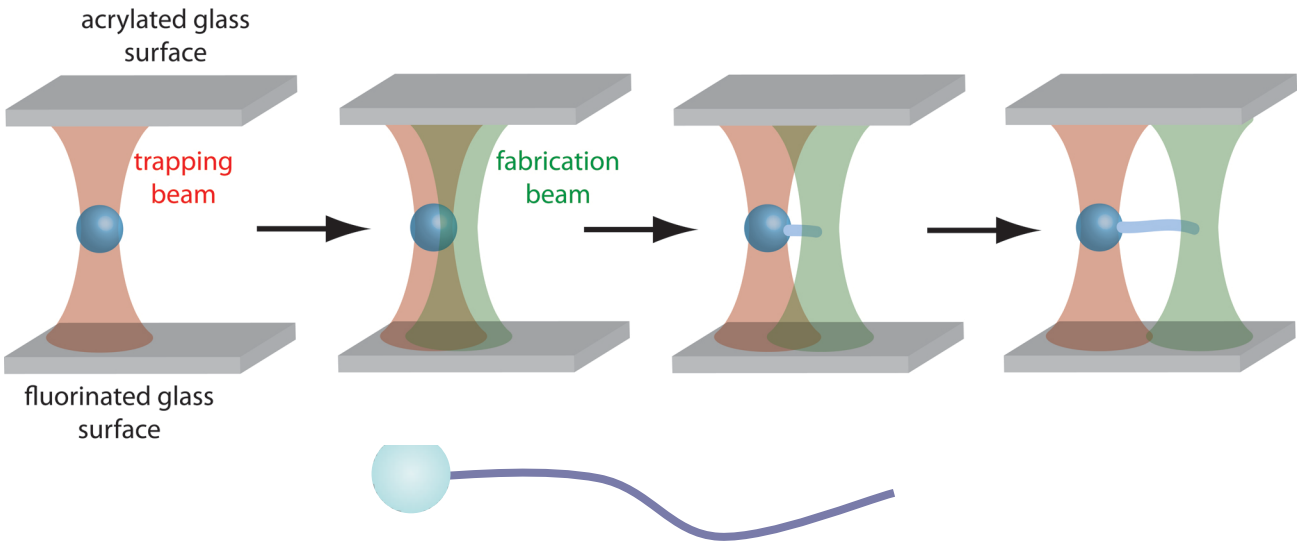
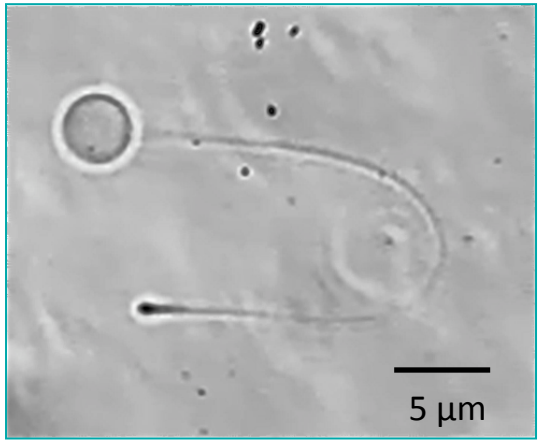
Fabrication of Microthreads – Method II

Creation of microtetherball and pole

Threading of a needle eye with microthread

Fabrication of Microthreads



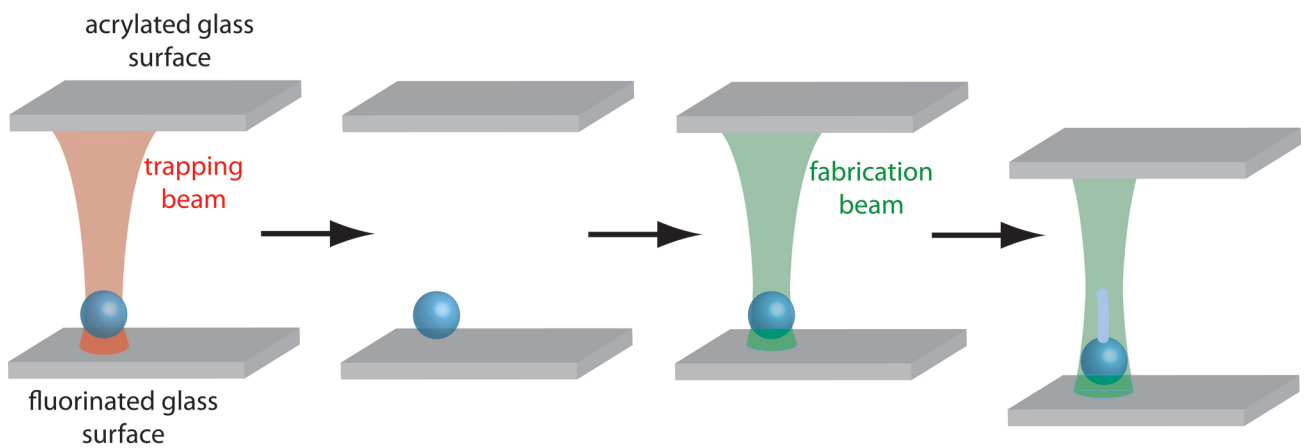


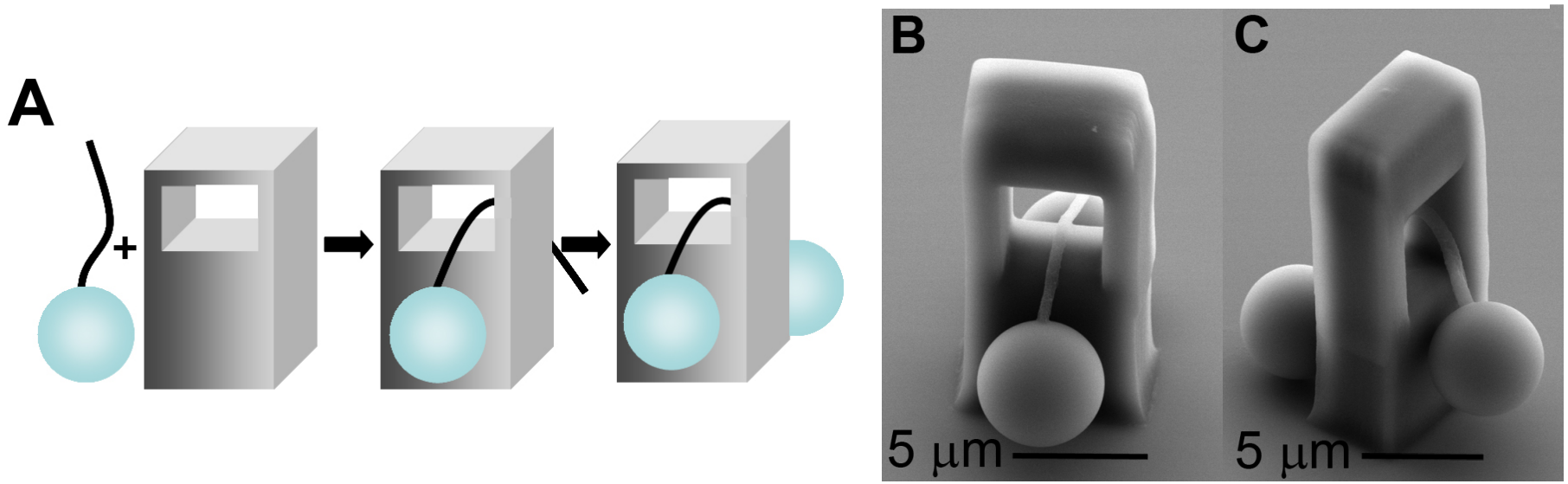
individual BSA microthread

Dawood, F.; Qin, S.; Li, L.; Lin, E. Y.; Fourkas, J. T. *Chem. Sci.* 2012, Advanced Article.

Fabrication of Microthreads – Method II

Method II





"needle" structure

Dawood, F.; Qin, S.; Li, L.; Lin, E. Y.; Fourkas, J. T. *Chem. Sci.* 2012, *3*, 2449.

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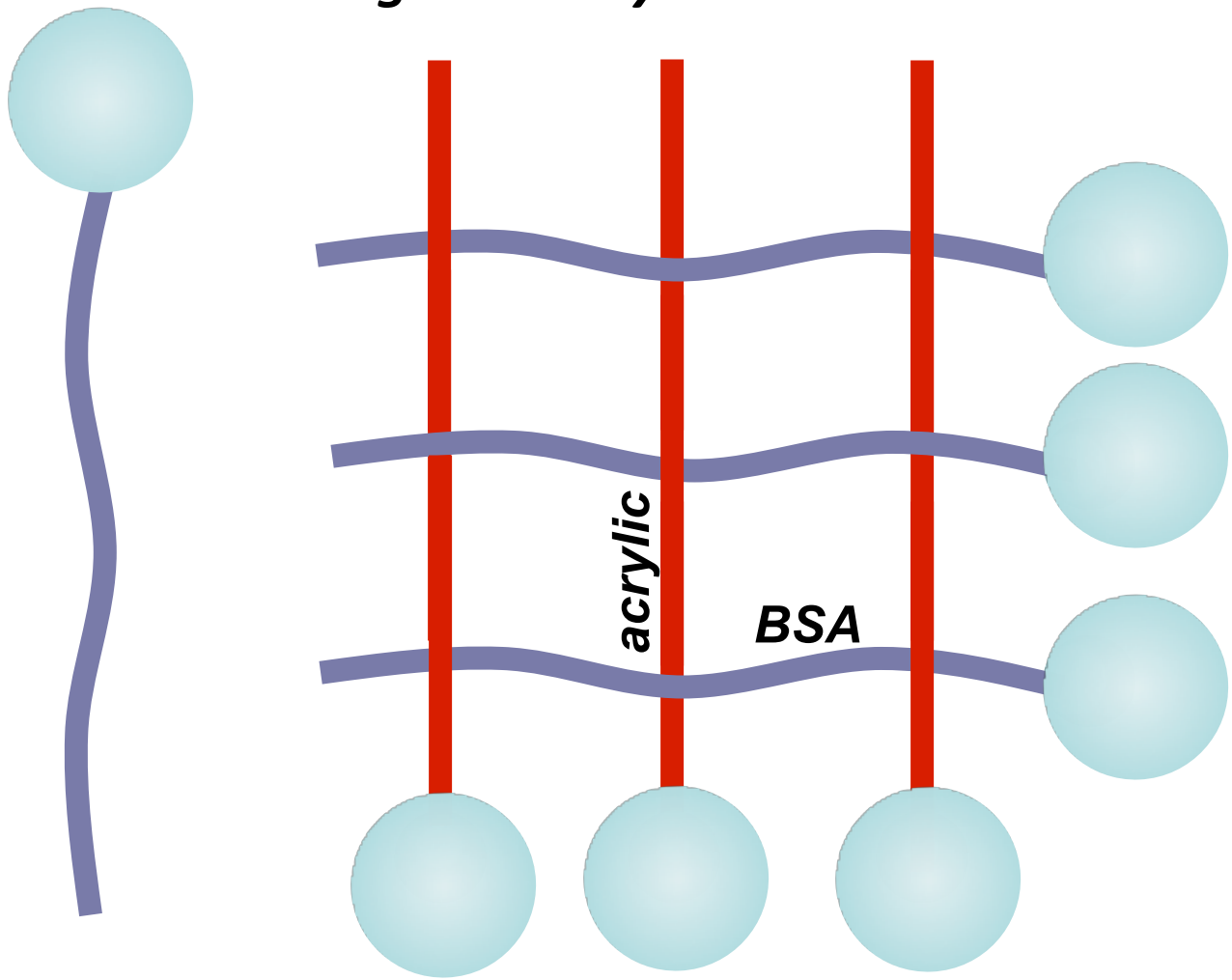
Microthreads of Multiple Materials

microweaving with acrylic and BSA microthreads



microweaving with microthreads

Dawood, F.; Qin, S.; Li, L.; Lin, E. Y.; Fourkas, J. T. *Chem. Sci.* 2012, *3*, 2449.

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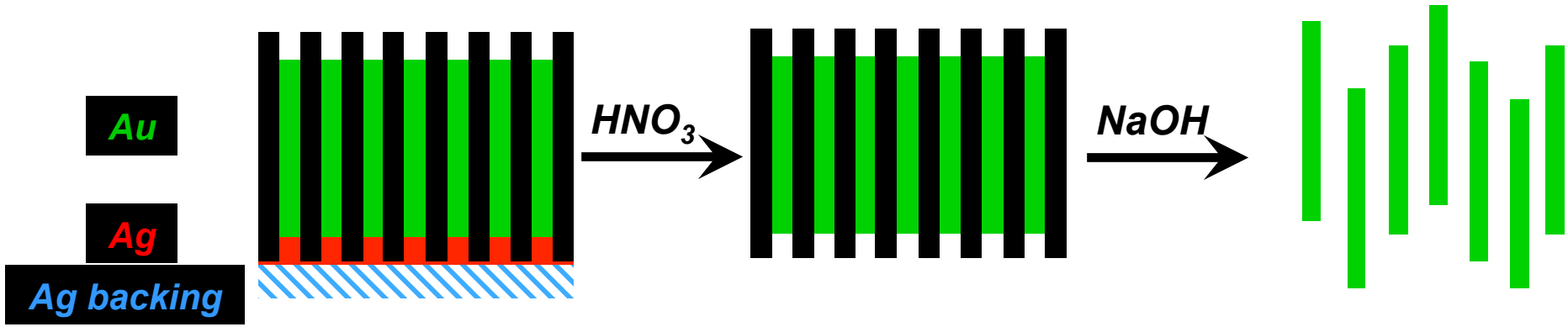
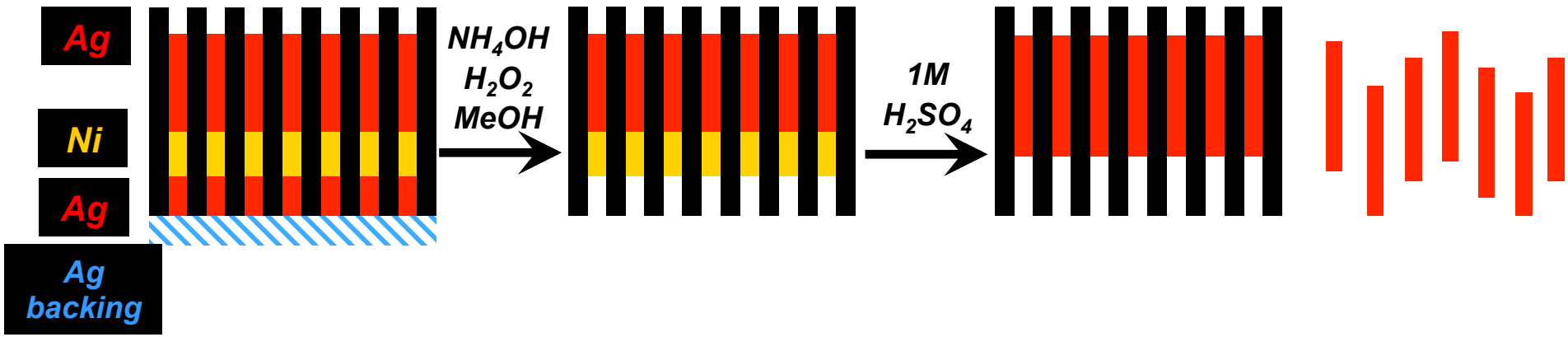
Template based Growth of Silver Nanowires

Use Anodic Aluminum Oxide (AAO) membranes

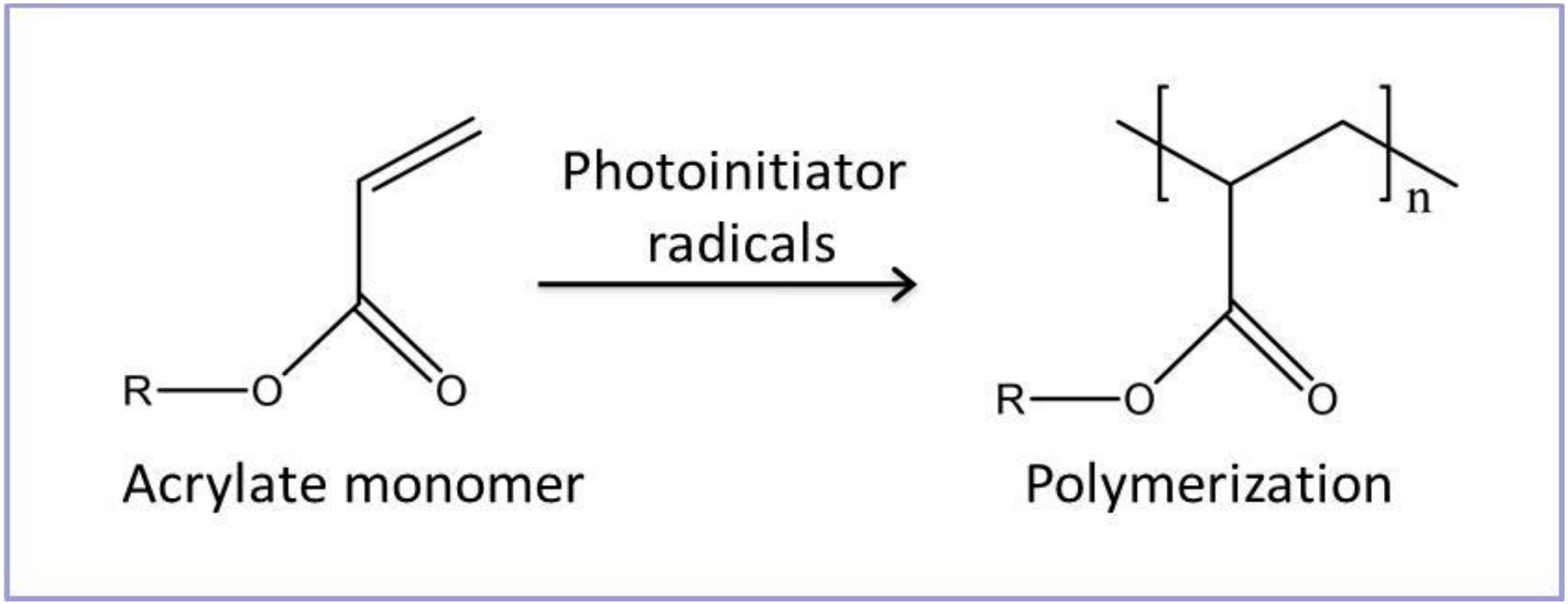




Gu, Z. et. al *Electrochem and Solid State Letters*; **2010**, *13*, D50.

UNCLASSIFIED

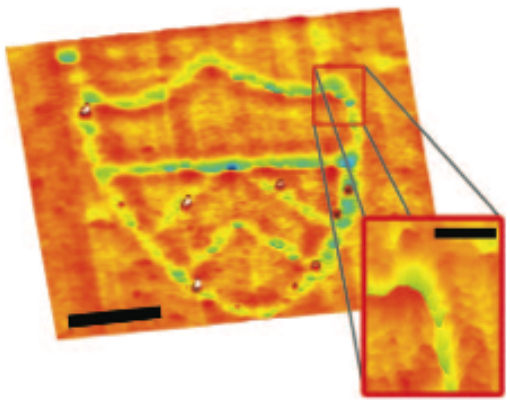
Polymerization Process



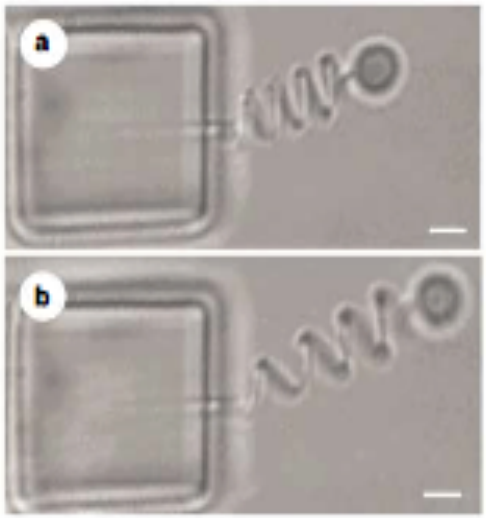
Optical Tweezers – General Applications

Manipulation - microfabrication, particle sorting, micromachines

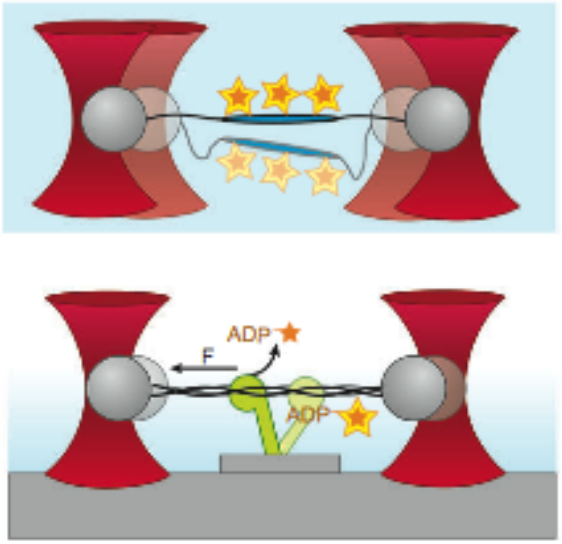
Measuring forces - molecular motors, tracking molecular motors



nanopatterning



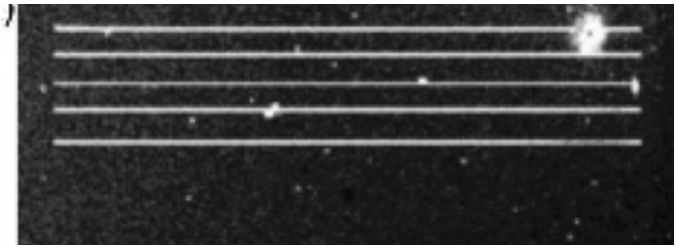
microoscillator



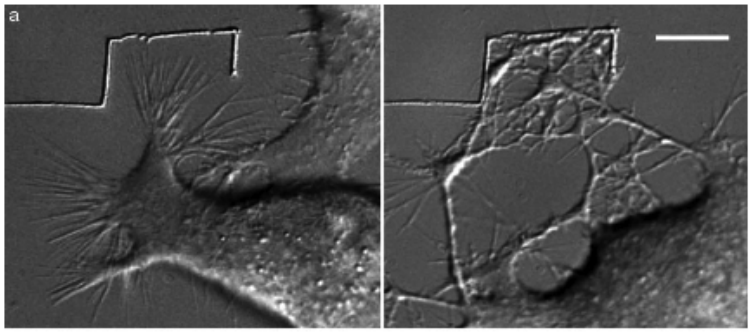
tracking myosin

McLeod, E.; Arnold, C. B. *Nature Nanotechnology* 2008, *3*, 413.
Kawata, S.; Sun, H.; Tanaka, T.; Takada, K. *Nature* 2001, *412*, 697-698.
Moffitt, J. R.; Chemla, Y. R.; Smith, S. B.; Bustamante, C. *Annu. Rev. Biochem.* 2008, *77*, 205–228.

MAP for Crosslinking Biomolecules



MAP of collagen



BSA structures can confine neuronal growth

Mask directed MAP of BSA

structures not as robust

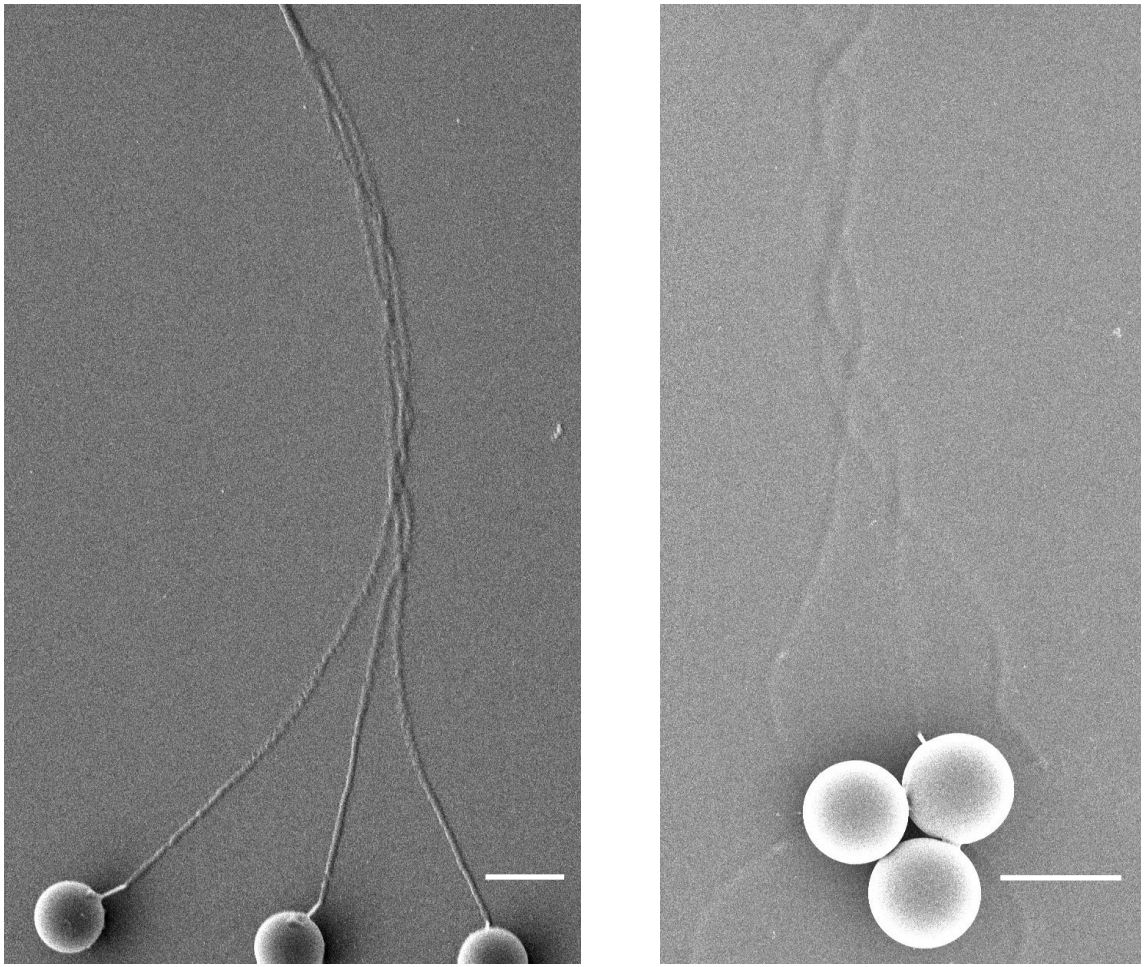
expensive

not ideal for secondary exposure

Campagnola, P. J. et. al. *Biomacromolecules* **2005**, *6*, 1465.
Shear, J. B. et. al. *PNAS* **2004**, *101*, 16105.
Kaehr, B.; Shear, J. B. *J.Am. Chem.Soc.* **2007**, *129*, 1904.

- This irreversible mechanism generates an electron deficient protein that may react with another protein's amino acid residue to form a covalent bond. It has been shown by others that this scheme generally favors residues containing olefins, dienes, aromatics, and heterocycle groups including tryptophan, tyrosine, or histidine.

Braiding



A microbraid constructed by manipulating microthreads using optical tweezers (scale bar 5 μm)

Dawood, F.; Qin, S.; Li, L.; Lin, E. Y.; Fourkas, J. T. *Chem. Sci.* 2012, *3*, 2449.

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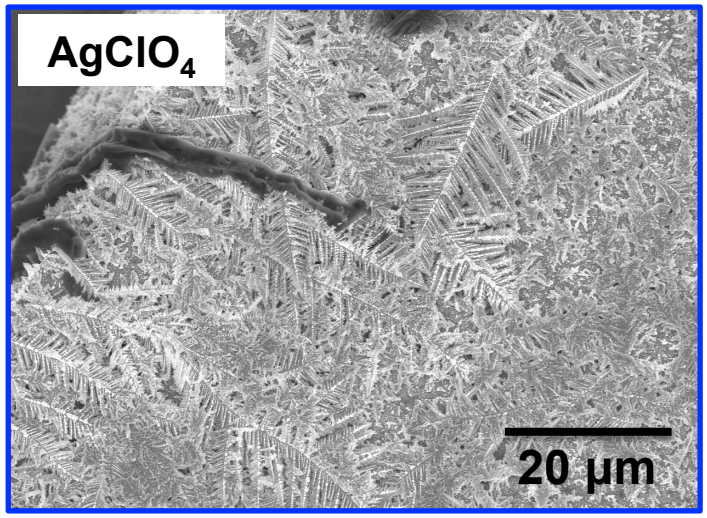
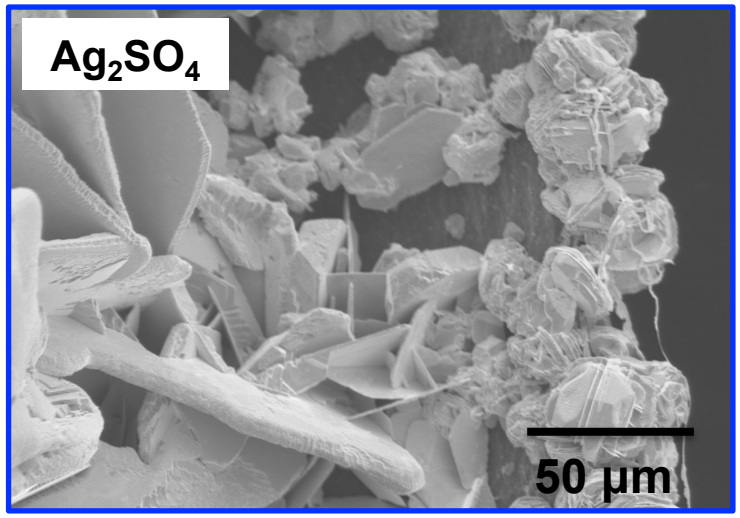
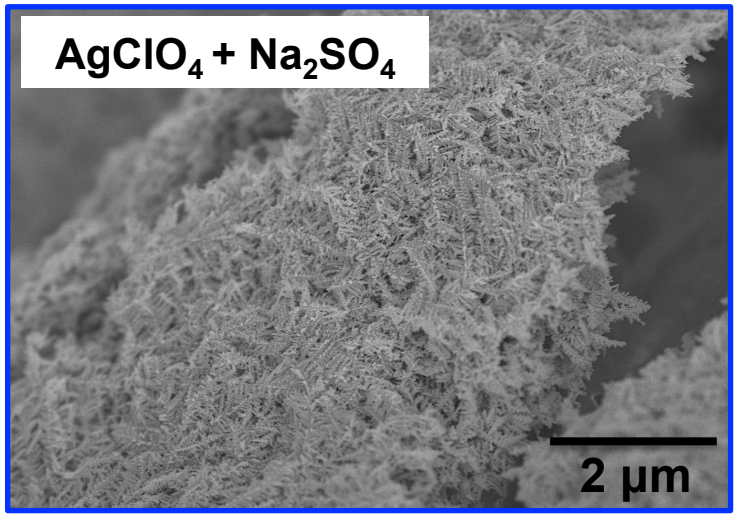
Anion Studies

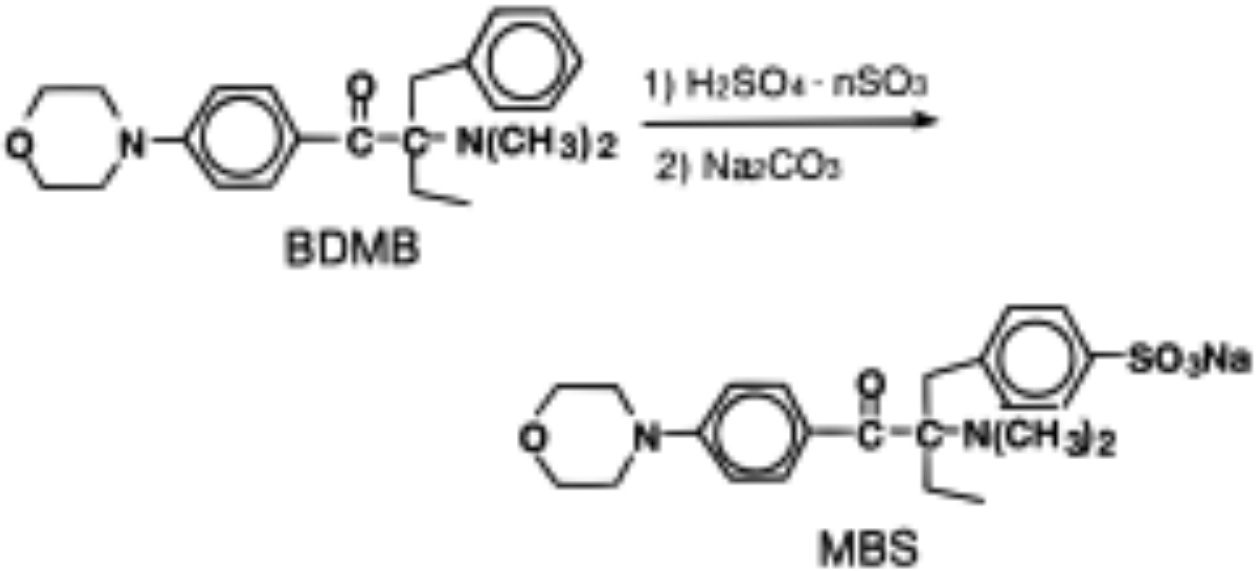


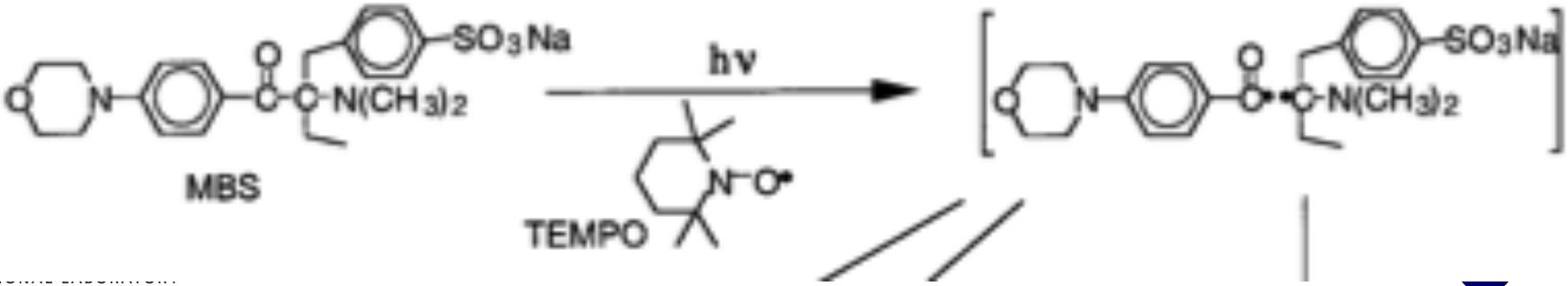




MBS

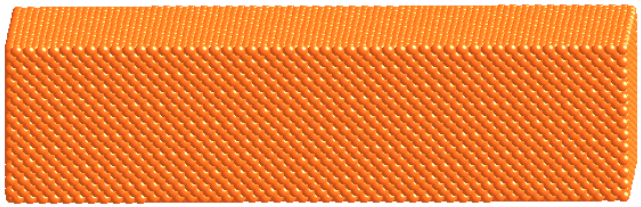
Scheme 1





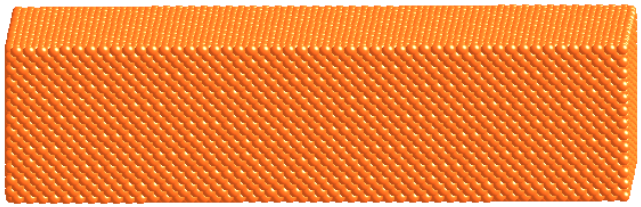
Synthesis of Nanocrystals and Nanomaterials

Top-down approaches



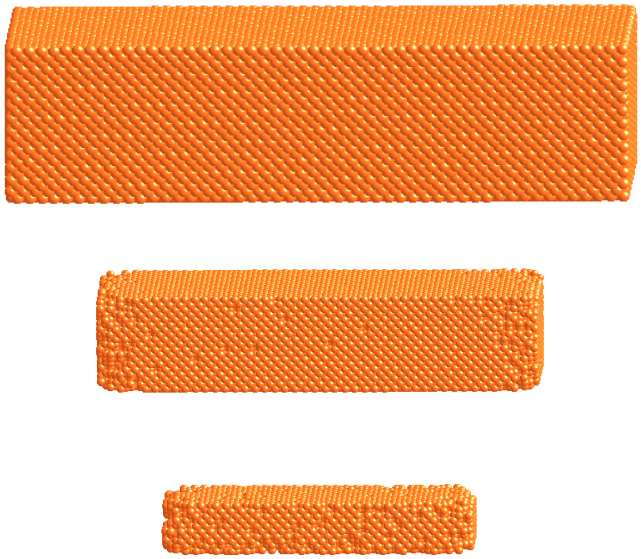
Synthesis of Nanocrystals and Nanomaterials

Top-down approaches



Synthesis of Nanocrystals and Nanomaterials

Top-down approaches



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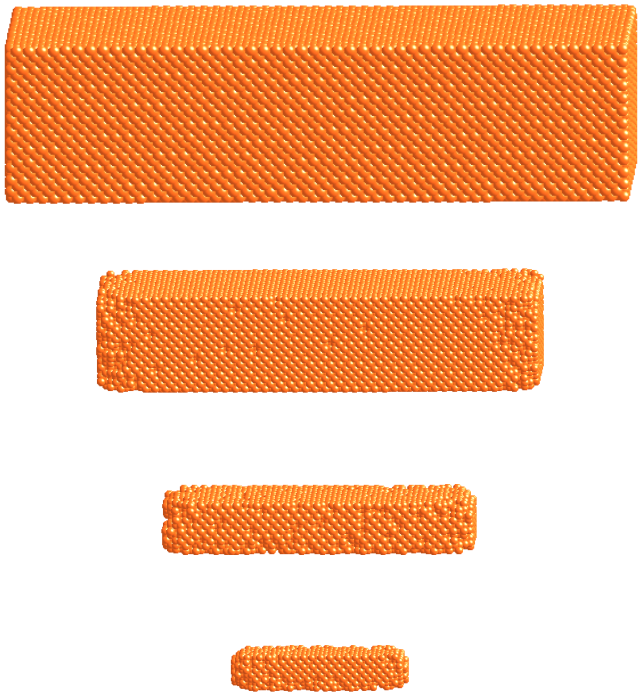
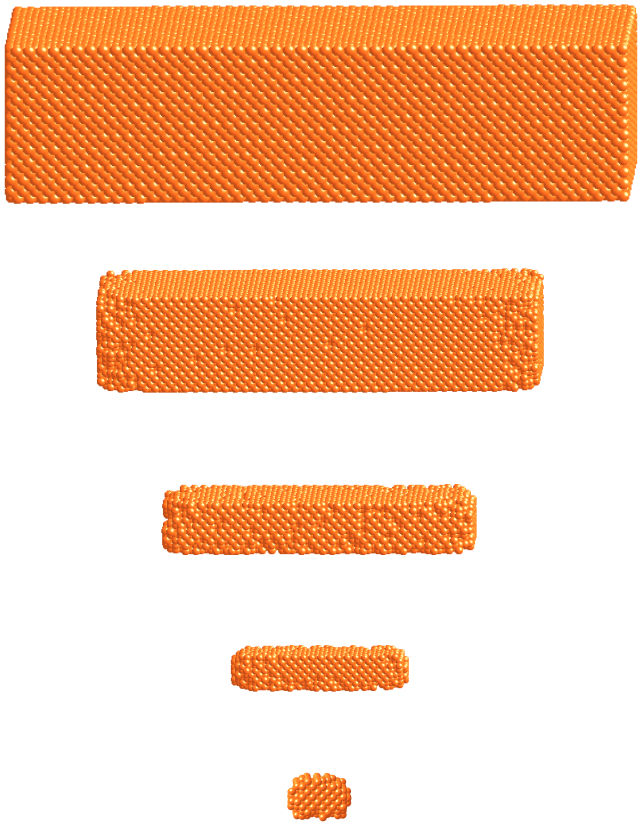
Top-down approaches



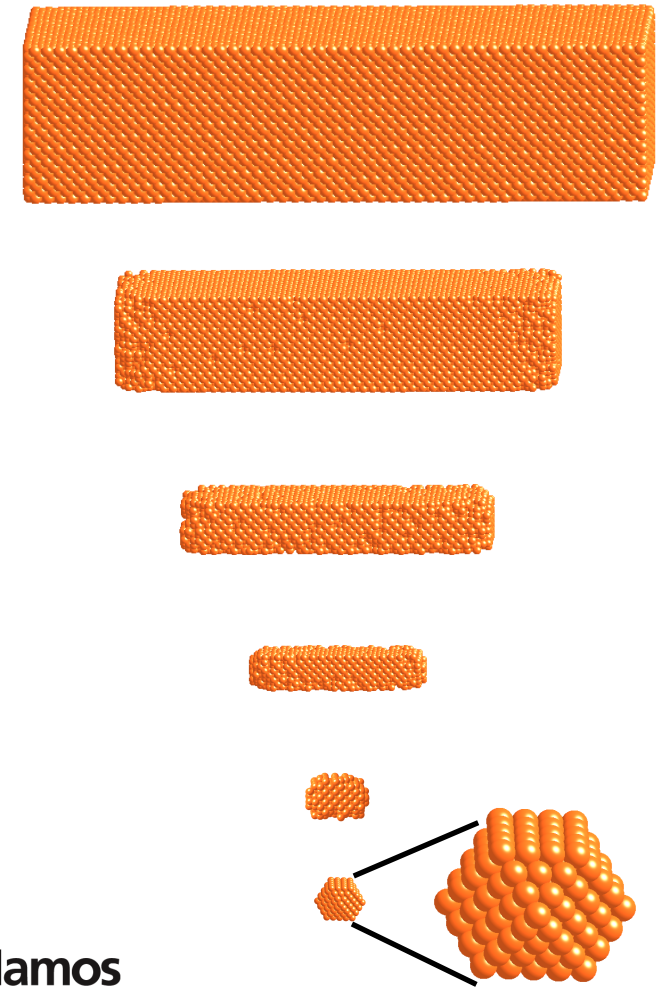
Synthesis of Nanocrystals and Nanomaterials

Top-down approaches



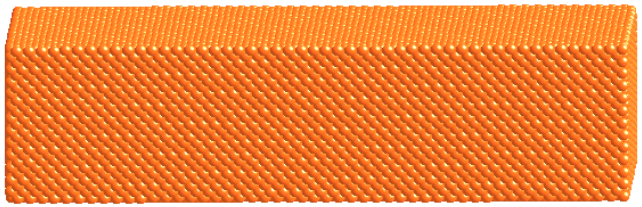
Synthesis of Nanocrystals and Nanomaterials

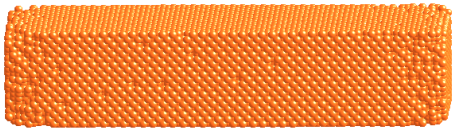
Top-down approaches

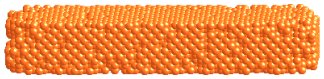


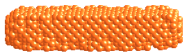
Synthesis of Nanocrystals and Nanomaterials

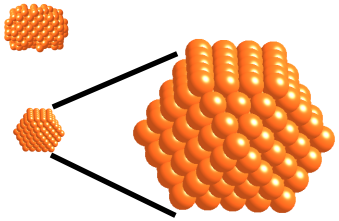
Top-down approaches









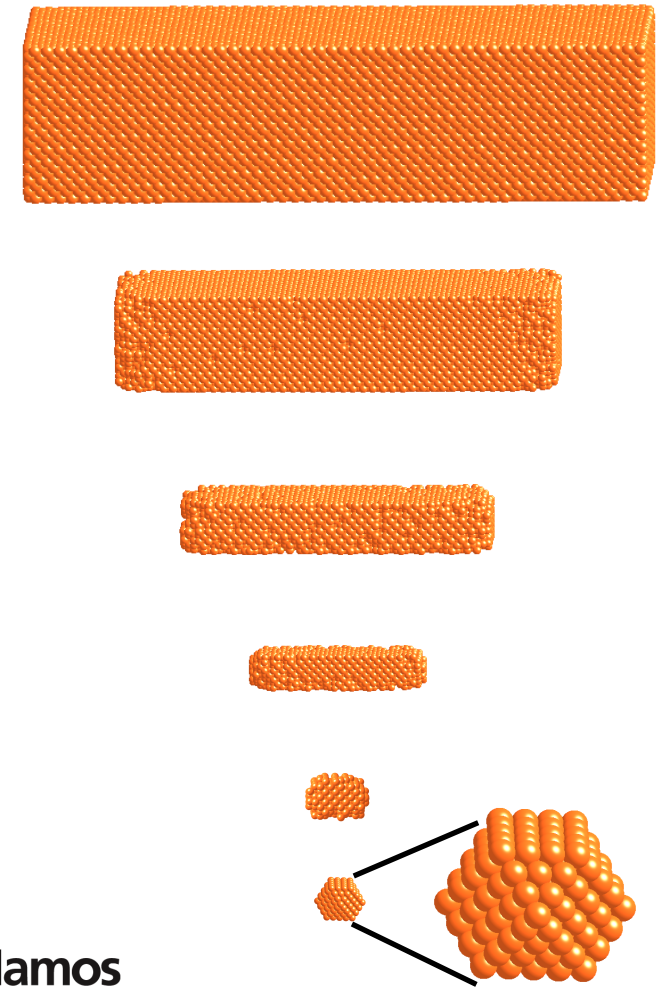


48-core concept chip from Intel

http://www.intel.com/pressroom/archive/releases/2009/20091202comp_sm.htm

Synthesis of Nanocrystals and Nanomaterials

Top-down approaches



48-core concept chip from Intel

requires specialized equipment

obtain thermodynamically stable product

http://www.intel.com/pressroom/archive/releases/2009/20091202comp_sm.htm

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Synthesis of Nanocrystals and Nanomaterials

Bottom-up approaches

http://www.intel.com/pressroom/archive/releases/2009/20091202comp_sm.htm

Synthesis of Nanocrystals and Nanomaterials

Bottom-up approaches

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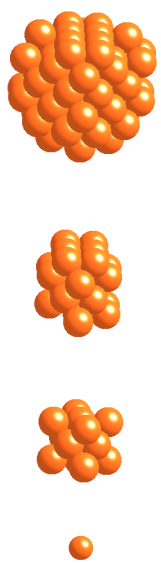
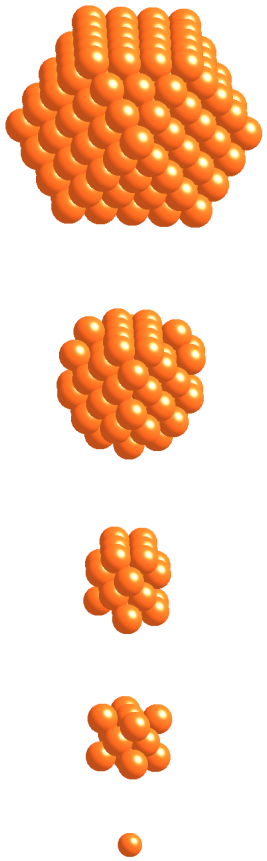


http://www.intel.com/pressroom/archive/releases/2009/20091202comp_sm.htm

Synthesis of Nanocrystals and Nanomaterials

Bottom-up approaches



uses mild synthetic conditions (low temperature)

obtain kinetically stable product

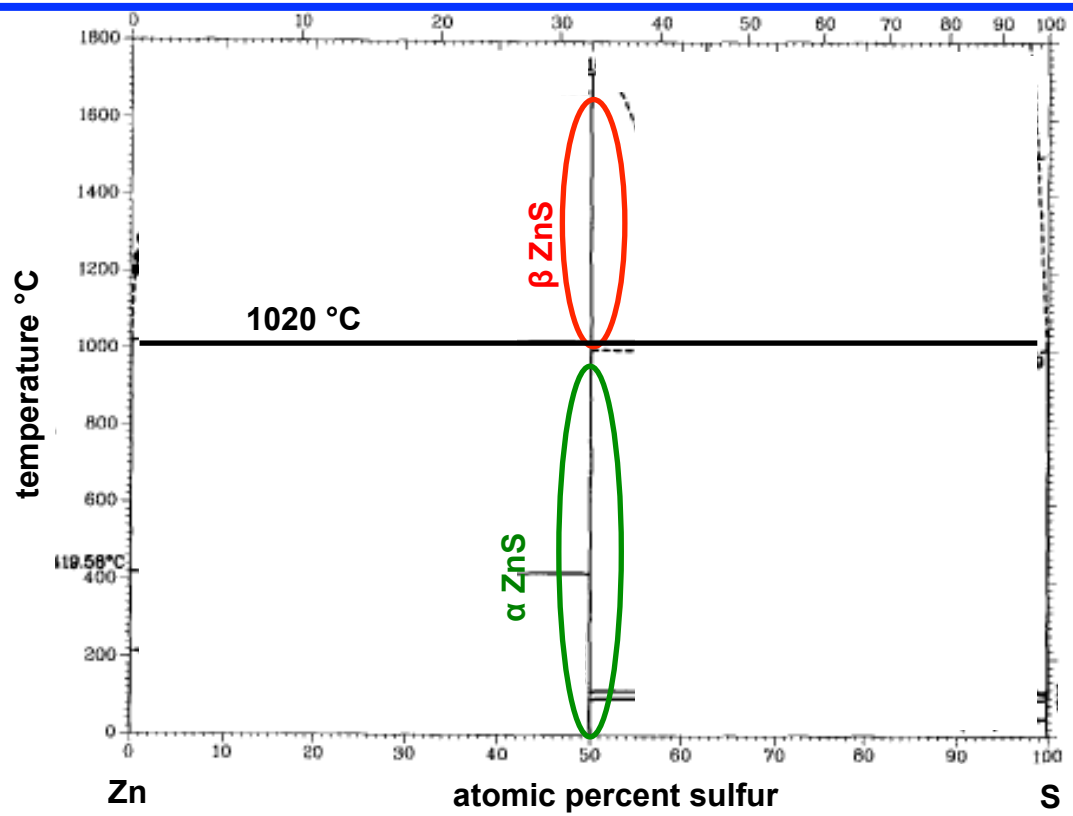
http://www.intel.com/pressroom/archive/releases/2009/20091202comp_sm.htm

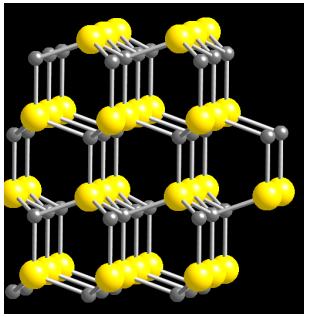
Polymorphism

2A + 2B ⟶ AB + AB

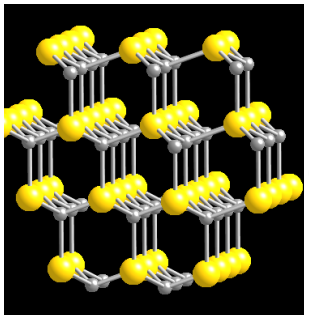
the ability of a solid to adopt different crystal structures that have the *same* composition

e.g. ZnS





β ZnS
(wurtzite)



α ZnS
(zinc blende)

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Sharma, R. C.; Chang, Y. A. *J. Phys. Equil.* **1996** *17* 261.

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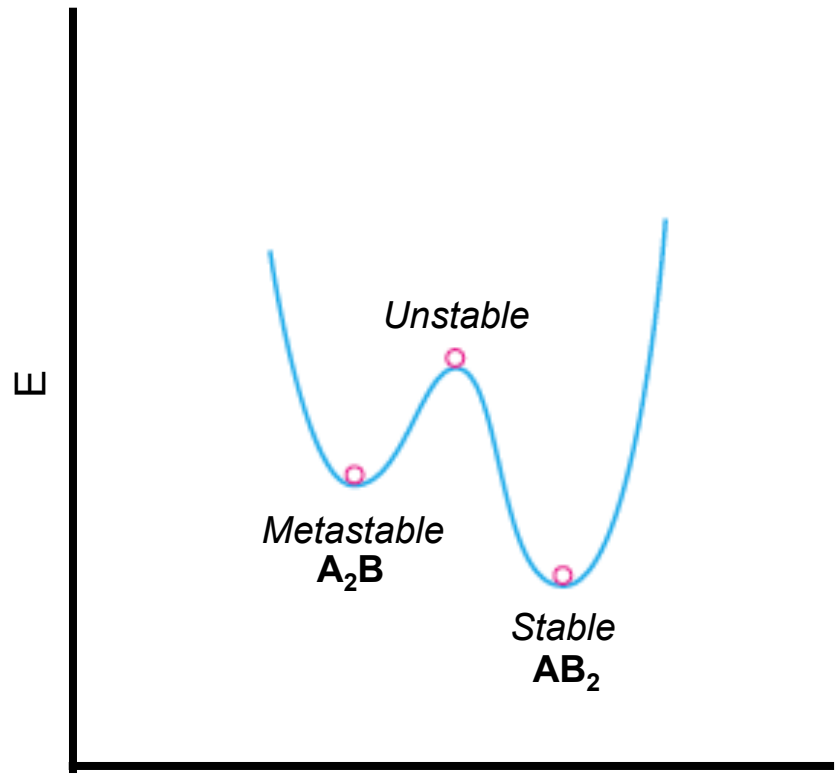
Metastable Phases

$$3A + 3B \longrightarrow A_2B + AB_2$$

Reactants → *Metastable* + *Stable*



Low(er) temperatures allow accessibility of phases that are difficult to synthesize

West, A. *Solid State Chemistry and its Applications* Wiley **2014**

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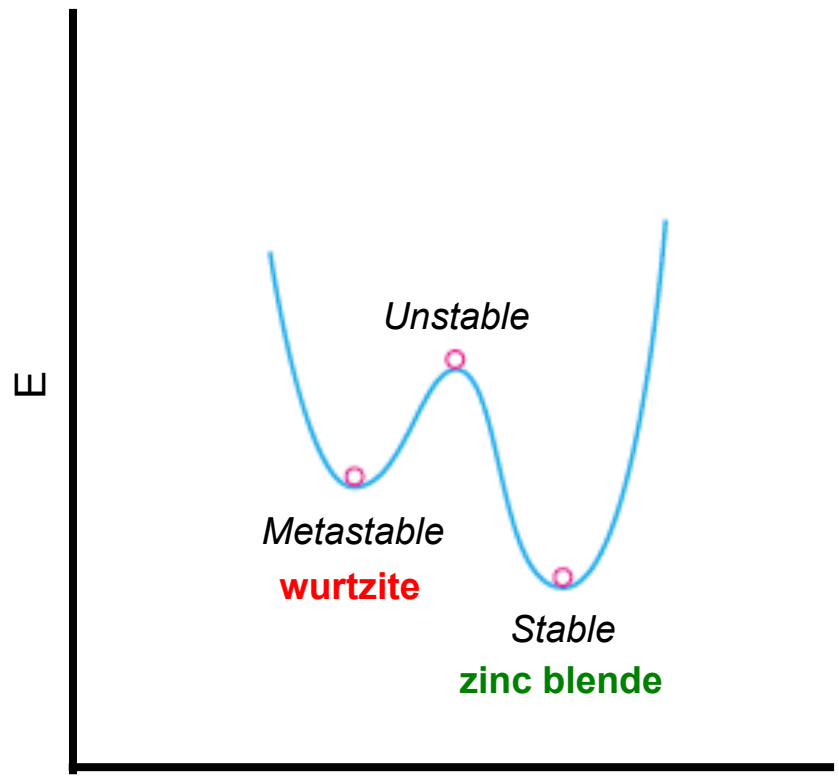
The ZnS System

$$2Zn^{2+} + 2S^{2-} \longrightarrow \text{wz ZnS} + \text{zb ZnS}$$

Reactants — *Metastable* — *Stable*

ZnS can adopt two crystal structures: **wurtzite** ***hcp*** (hexagonal close packed)

zinc blende ***ccp*** (cubic close packed)



Sharma, R. C.; Chang, Y. A. *J. Phys. Equil.* **1996** *17* 261.

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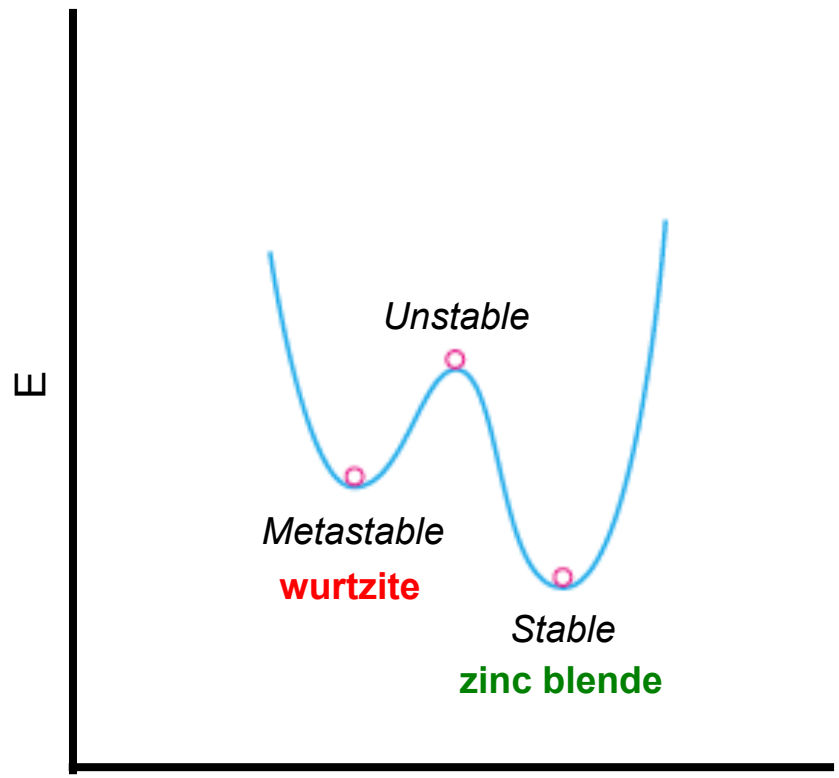
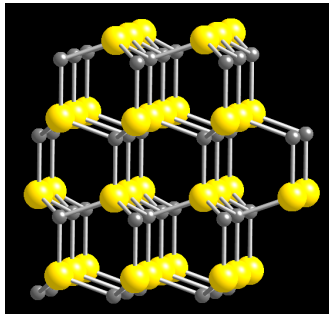
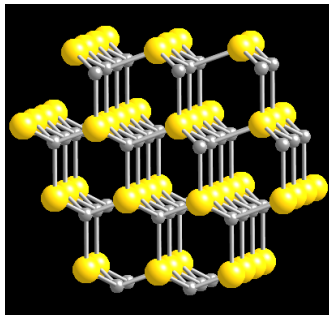




wurtzite
hcp



zinc blende
ccp

Sharma, R. C.; Chang, Y. A. *J. Phys. Equil.* **1996** *17* 261.

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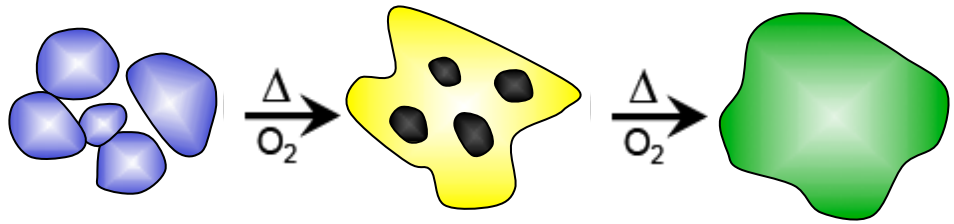
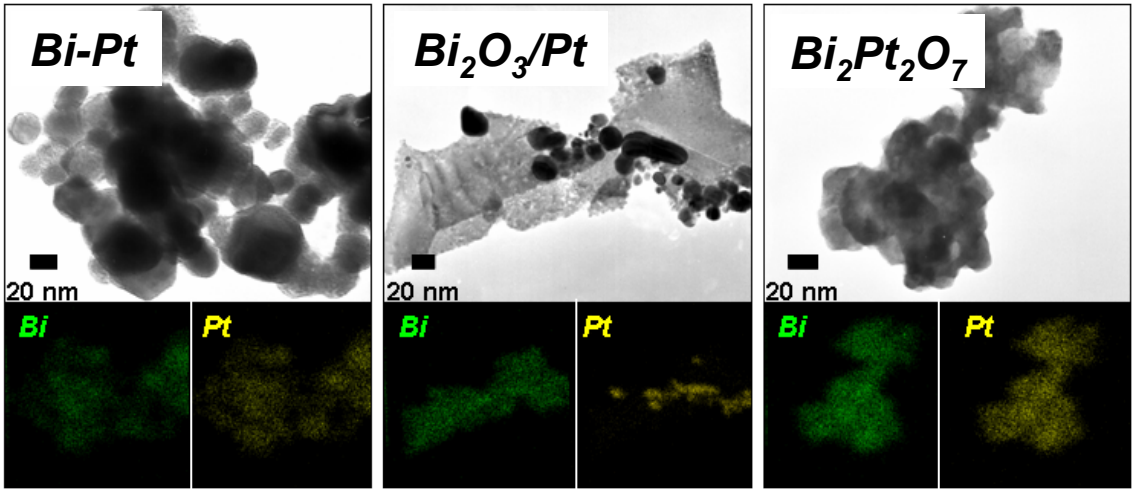
Expanding to $Bi_2Pt_2O_7$ System



Intermetallic nanoparticles | *Metal/Oxide nanocomposite* | *Multi-metal oxide nanoparticles*



$$\text{Bi-Pt} \xrightarrow[O_2]{\Delta} Bi_2O_3 / Pt \xrightarrow[O_2]{\Delta} Bi_2Pt_2O_7$$

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Dawood, F.; Leonard, B.M.; Schaak, R. E. *Chem. Mater.* **2007**, *19*, 4545-4550.

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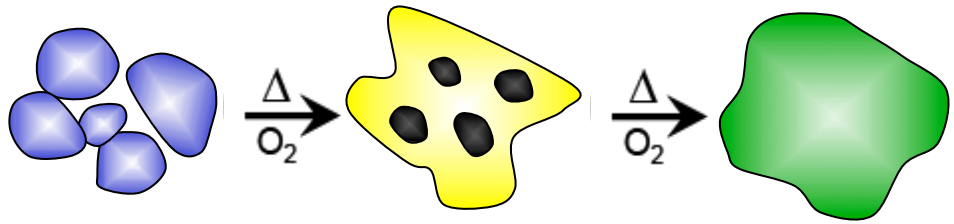
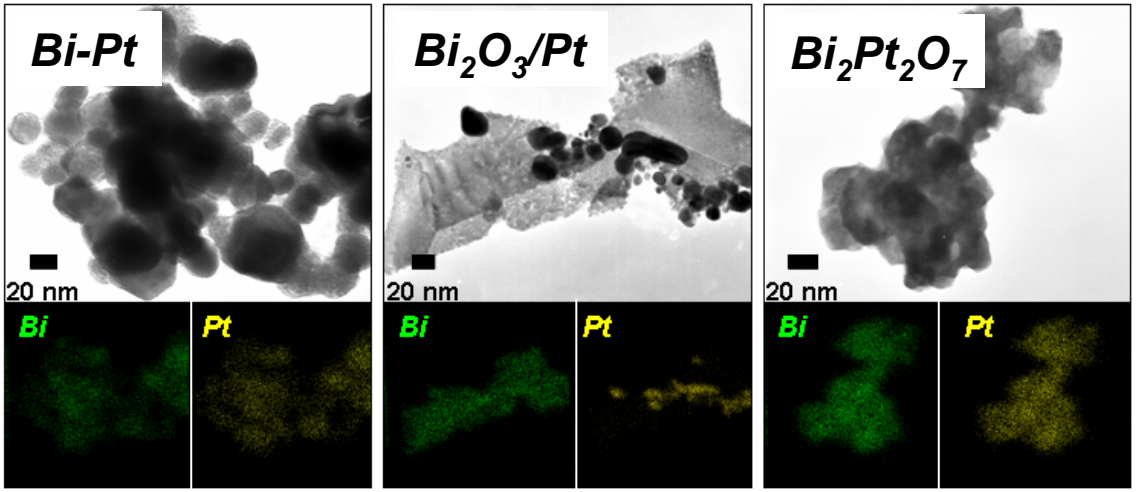
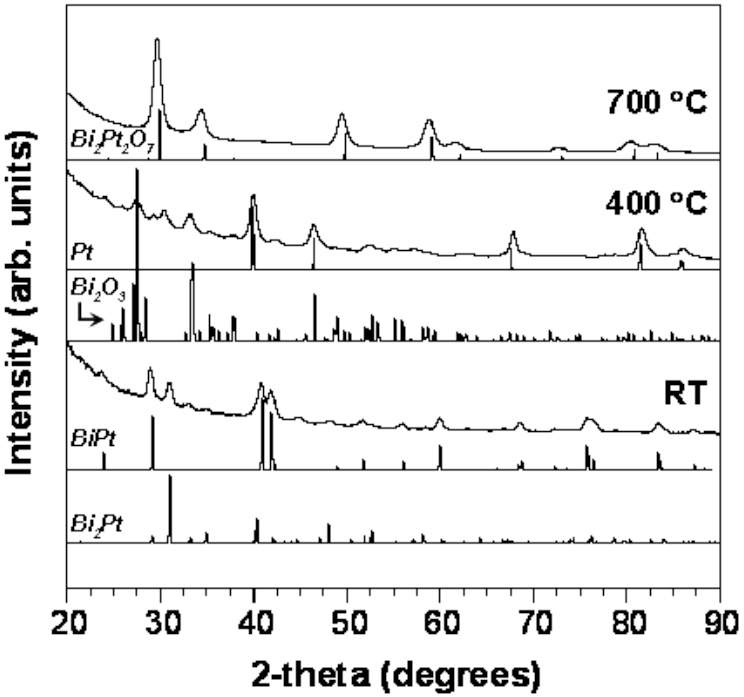
Expanding to $Bi_2Pt_2O_7$ System



Intermetallic nanoparticles | *Metal/Oxide nanocomposite* | *Multi-metal oxide nanoparticles*





Bi-Pt $\xrightarrow[O_2]{\Delta}$ **Bi_2O_3 / Pt** $\xrightarrow[O_2]{\Delta}$ **$Bi_2Pt_2O_7$**

The intermediate nanocomposite mimics a supported catalyst

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Dawood, F.; Leonard, B.M.; Schaak, R. E. *Chem. Mater.* **2007**, *19*, 4545-4550.

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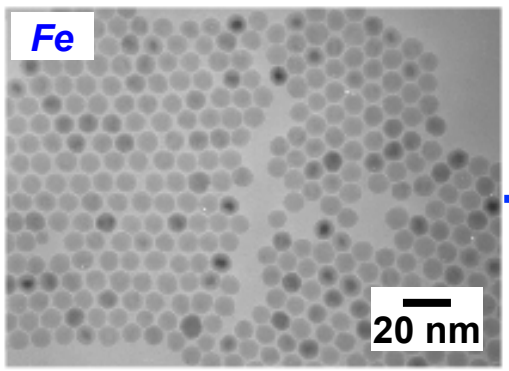
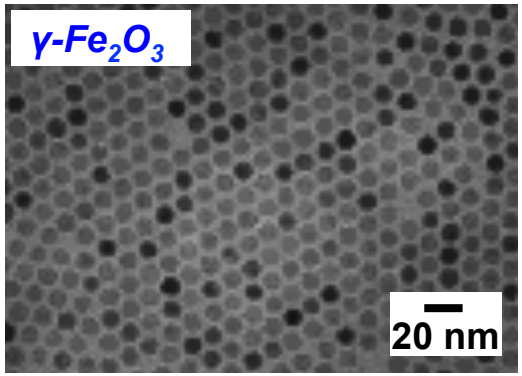
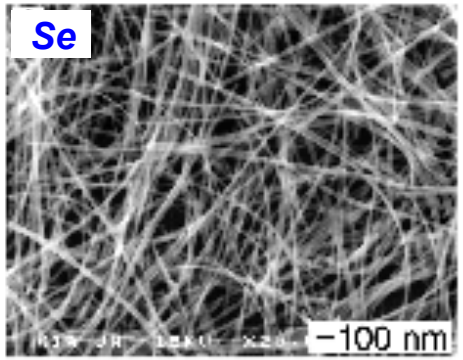
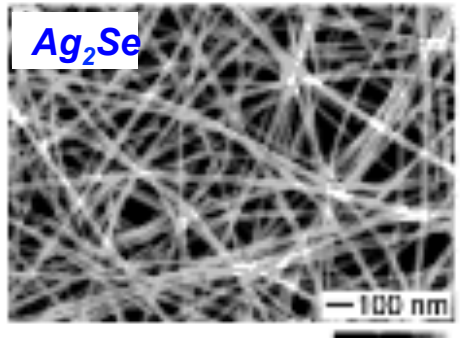
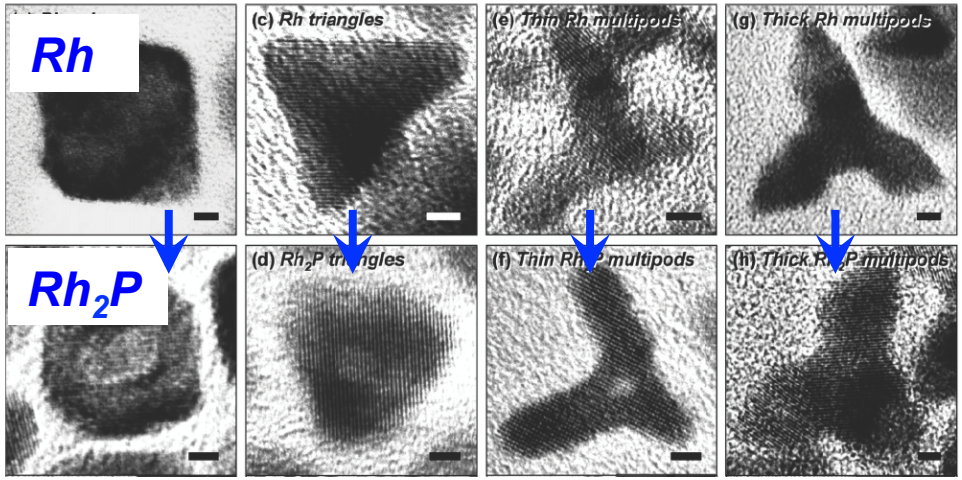
2. Morphological (Shape) Templating











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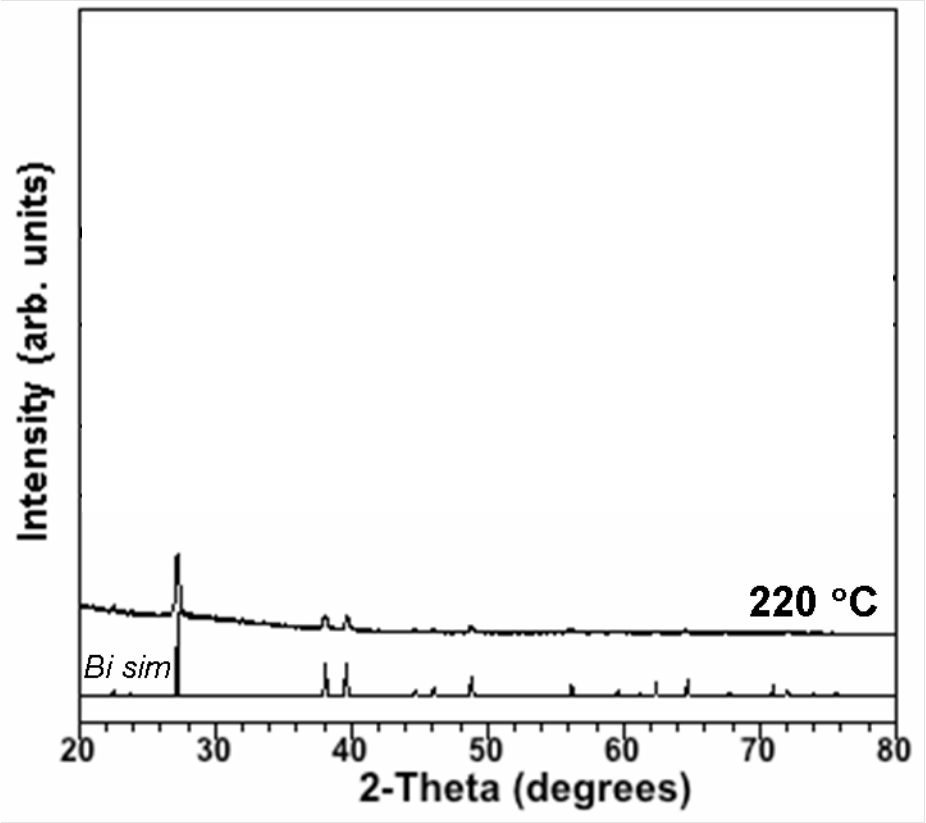
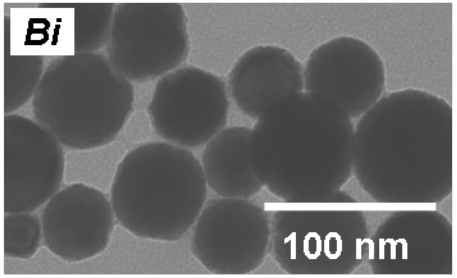
Two-Step Conversion Chemistry

$$Bi \rightarrow NiBi \rightarrow Ni_3Bi_2S_2$$





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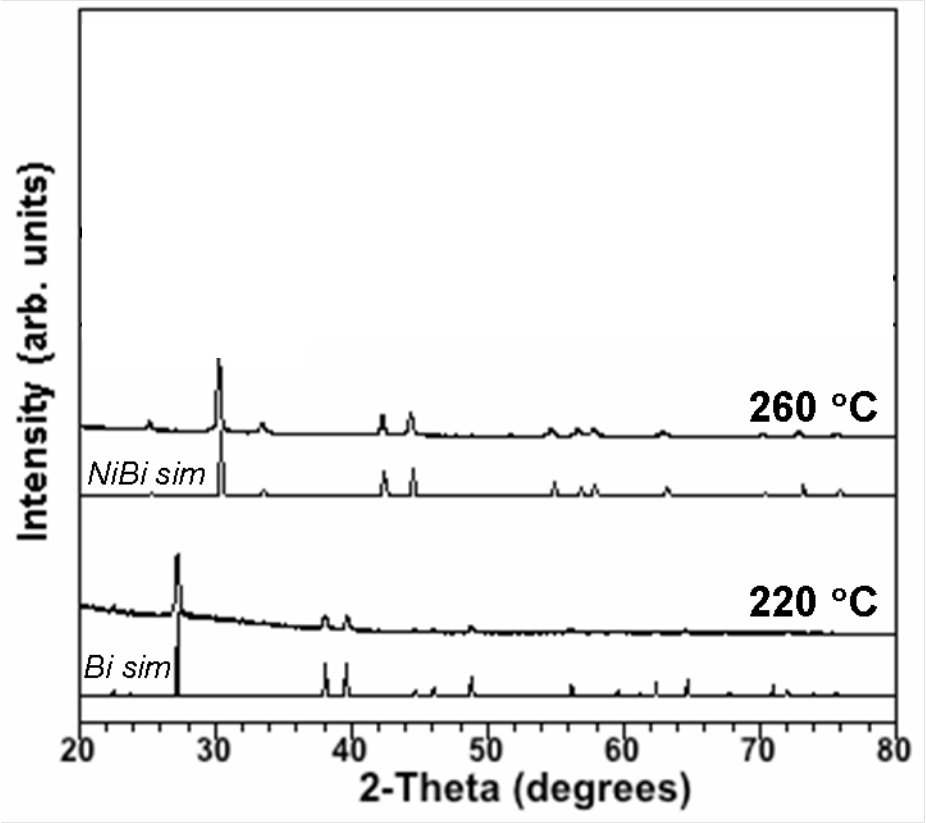

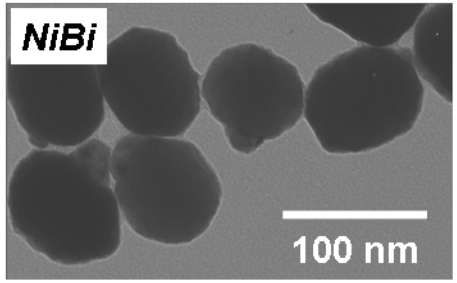

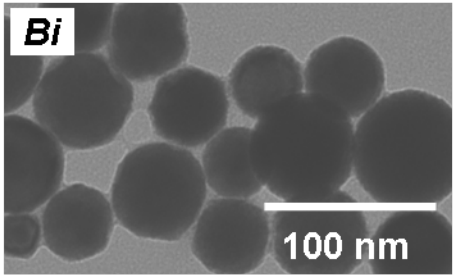

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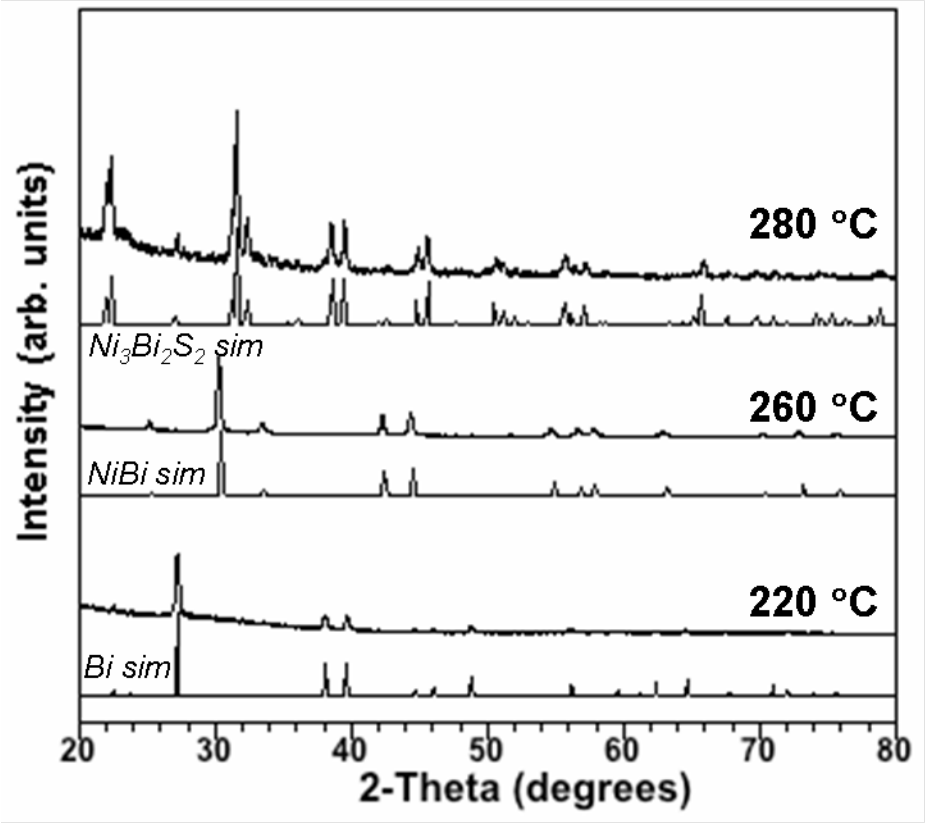

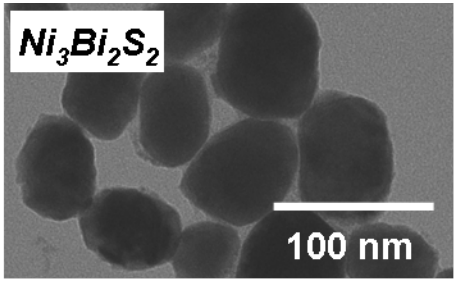

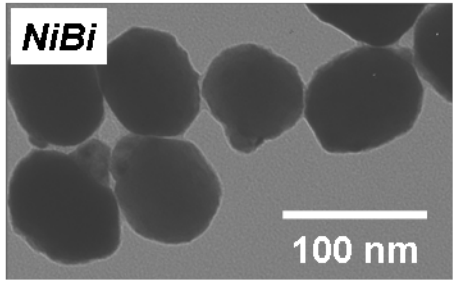

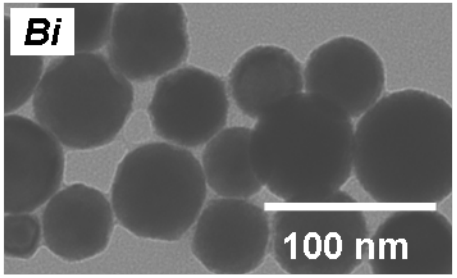

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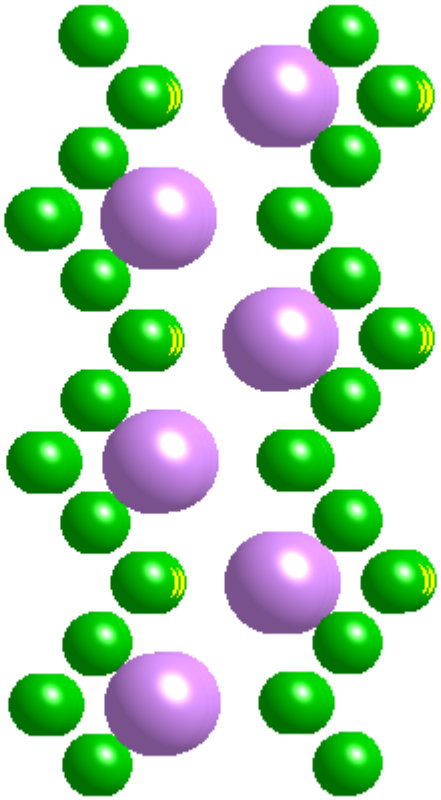

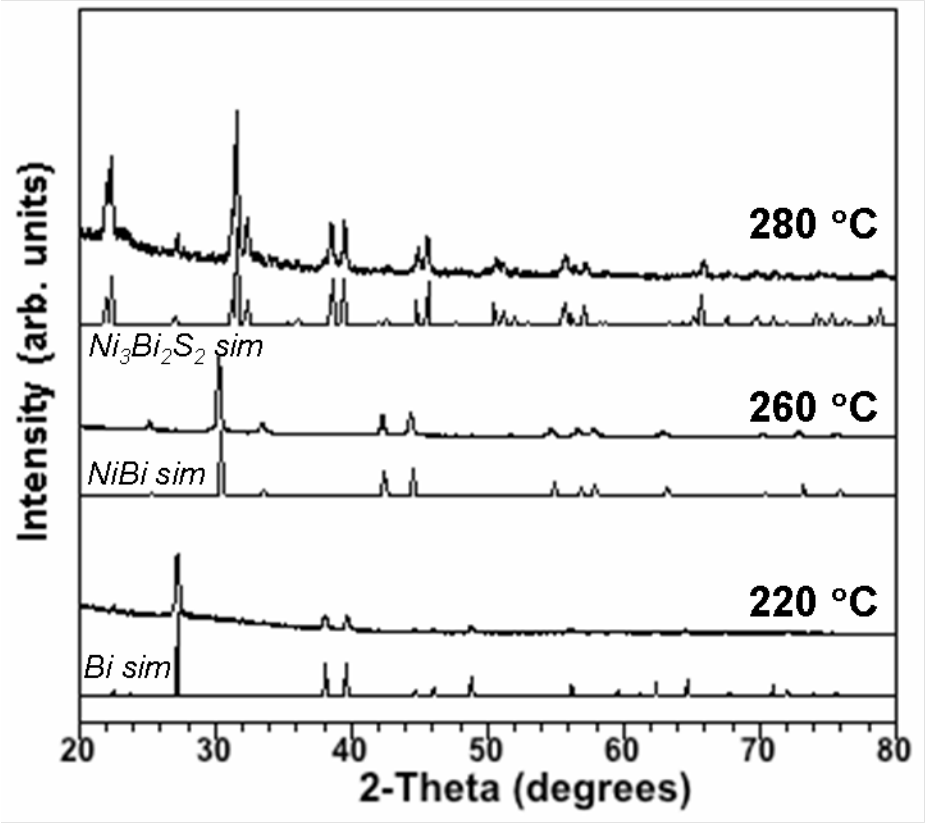

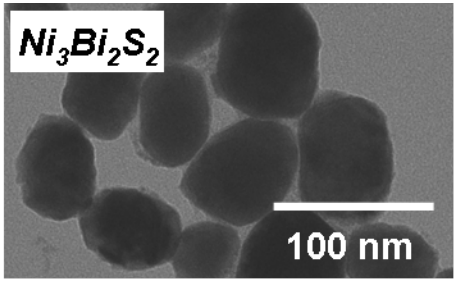

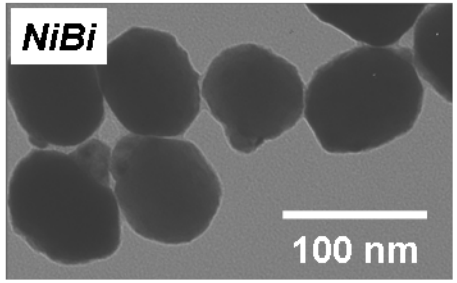

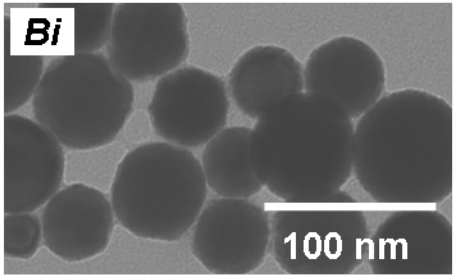

$Ni_3Bi_2S_2$ belongs a family of **mixed metal chalcogenides** that have not been studied extensively, but have the potential to have interesting properties due to their **zigzag chains of short metal-metal bonds within the crystal structure**

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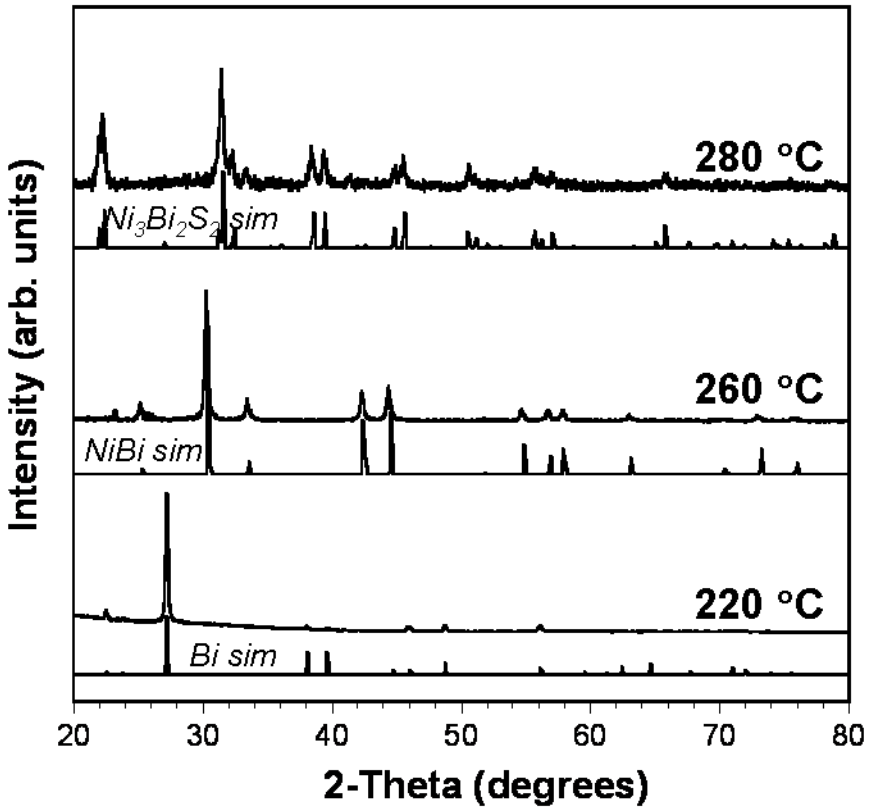
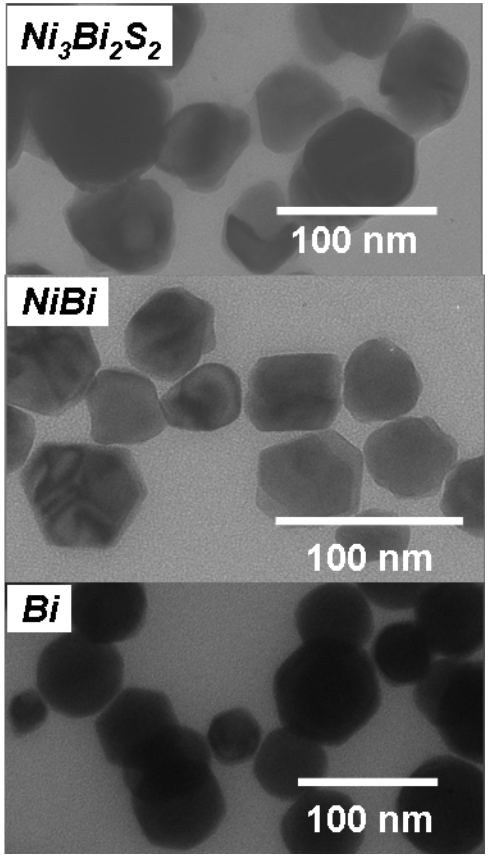
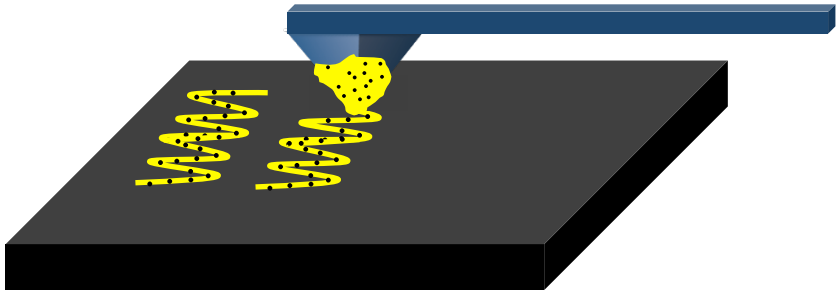
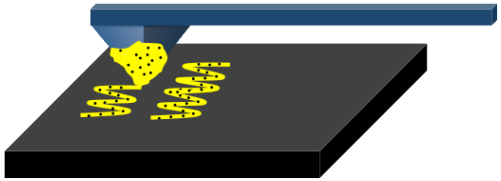
Conversion of Bi platelets





XRD patterns of Bi and NiBi show ***preferred orientation*** *that would be expected for* ***anisotropic particles****. The XRD pattern of $Ni_3Bi_2S_2$ shows no preferred orientation that agrees with the morphology of the resulting nanoparticles as seen by TEM.*